187. *Organic Sulphur Compounds. Part XXXI. Action of Heat on Some Free Radicals with Special Reference to the Free Phenylthiyl Radical.*

By ALEXANDER SCHÖNBERG and AHMED MUSTAFA.

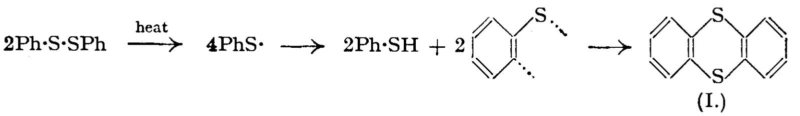
When diphenyl disulphide is heated at 270°, thiophenol and diphenylene disulphide (I) (thianthren) are formed in good yield, believed to be produced from the free PhS· radical by disproportionation (see Scheme A). The formation of thiophenol or thiocresol by the heating of *αβ*-bisphenylthiostilbene (II*a*) or its analogues is explained similarly.

At 270°, reactions according to the Schemes (C) and (D) take place; they furnish further evidence for the tendency of free radicals to stabilise by disproportionation.

SOME disulphides [*e.g.*, diphenyl disulphide and bisthionaphthoyl disulphide $(C_{10}H_7\cdot CS\cdot S\cdot)_2$] undergo with diphenyldiazomethane, hexaphenylethane, metal ketyls, metallic silver, and triphenylphosphine reactions which lead to a cleavage of the ·S·S· group (Schönberg, Rupp, and Gumlich, *Ber.*, 1933, **66**, 1932; Schönberg, *Ber.*, 1935, **68**, 163). The question arises how these reactions are to be explained. One may argue (*a*) that in these aromatic disulphides the S–S linkage is abnormally weak (when compared with that in, *e.g.*, dimethyl disulphide) and that it is broken in these particular reactions; but it is also possible (*b*) that, especially at high temperatures, these aromatic disulphides dissociate with the formation of free radicals containing univalent sulphur (RS·SR $\rightleftharpoons$ 2RS·) and that the above cleavages are brought about by the action of free radicals and not by the action of disulphides.

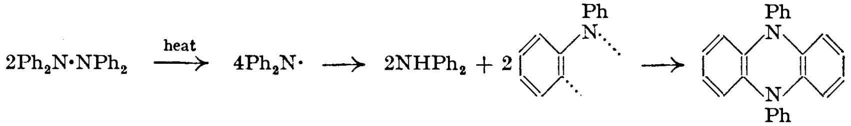
If the view (*a*) is accepted, then it is easy to imagine that in solution the " active " molecules (*i.e.*, only a small proportion of the total number) are dissociated to free radicals. Contrary to the views previously accepted (Lecher, *Ber.*, 1925, **58**, 417), it was pointed out for the first time by Schönberg (*Trans. Faraday Soc.*, 1934, **30**, 17; Schönberg *et al.*, *loc. cit.*) that diphenyl disulphide and related substances are capable of forming free arylthiyl radicals in hot solution. The dissociation theory of disulphides explains *inter alia* the thermochromic properties of diphenyl disulphide and the fact that its hot solutions do not obey Beer's law (Rupp, *Ber.*, 1933, **66**, 1933).

Pyrolysis should be a useful tool in deciding whether the formation of free radicals from disulphides actually takes place, taking into consideration the tendency of free radicals to stabilise according to the principle of disproportionation (see Scheme B, which shows the disproportionation reaction of diphenylnitrogen as formulated by Wieland, *Annalen*, 1911, **381**, 200). On the basis of the disproportionation theory, the formation of thiophenol and thianthren (I) from diphenyl disulphide at higher temperatures is to be expected, and this reaction actually occurs at 270°. Attention is drawn to the similiarity between Schemes (A) and (B); this analogy is a further indication that diphenyl disulphide forms free radicals at high temperatures, as do the tetra-arylhydrazines.



(I.)

(A)



(B)

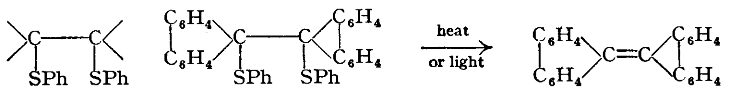
We have also found that, when αβ-bisphenylthiostilbene (II*a*) is heated at 270°, tolan is formed together with thiophenol, believed to be the stabilisation product of Ph·S·.

The formation of thiophenol was also observed in the case of *αβ-bisphenylthio-αβ-dicumylethylene* (II*c*). The formation of thio-*p*-cresol was observed when di-*p*-tolyl disulphide was heated at 270° and in the pyrolysis of *αβ-bis-*p*-tolylthiostilbene* (II*b*). In all these cases, the formation of thio-phenol or -*p*-cresol should be explained as occurring *via* the free arylthiyl radical.

Of the ethylenes previously mentioned, (II*a*) had been obtained by the action of thiophenol on benzoin in the presence of glacial acetic and hydrochloric acid (Posner, *Ber.*, 1902, **35**, 506) and the new ethylenes were prepared analogously.

$$R'{\cdot}C(SR){:}CR'{\cdot}SR$$
(II*a*; $R = R' = Ph$. II*b*; $R = p\text{-}Me{\cdot}C_6H_4$, $R' = Ph$. II*c*; $R = Ph$, $R' = p\text{-}C_6H_4{\cdot}CHMe_2$.)

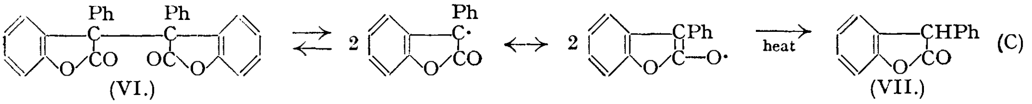
Recently, it has been shown that disulphides, believed to undergo dissociation into free radicals, react with olefins. Diphenyl disulphide, however, proved to be entirely without action on *cyclo*hexene at 180° (Bloomfield, *J.*, 1947, 1549). In this connection, it should be pointed out that substances containing the group (III) must be expected to be more or less thermolabile. For instance, (IV) is converted into (V) in boiling toluene in the dark and in benzene at room temperature in the presence of light (Schönberg and Stolpp, *Annalen*, 1930, **483**, 90). Therefore, the fact that diphenyl disulphide does not add to the double bond with the

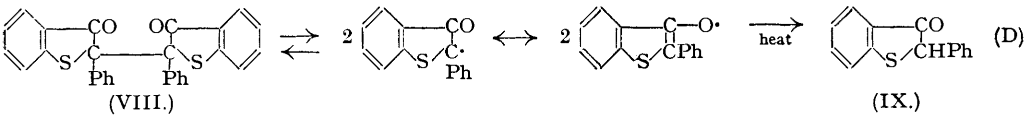


(III.) (IV.) (V.)

formation of substances stable at 180°, cannot be used as an argument against the theory that diphenyl disulphide and its analogues dissociate at higher temperatures.

Action of Heat on 2 : 2'-*Diketo*-3 : 3'-*diphenyl*-3 : 3'-*dicoumaranyl* (VI) *and* 2 : 2'-*Diphenylthioindigo-white* (VIII).—In connection with the above disproportionations, to which free radicals are liable, we have investigated the two substances (VI) and (VIII) which are known, in solution, to form free radicals that may be regarded as resonance hybrids and therefore as compounds containing a tervalent carbon atom or a univalent oxygen atom (Löwenbein and Simonis, *Ber.*, 1924, **57**, 2040; Kalb and Baeyer, *Ber.*, 1913, **46**, 3879). We have found that (VI) and (VIII) form the corresponding reduction products, namely, the lactone of *o*-hydroxydiphenylacetic acid (VII) and 3-keto-2-phenyl-2 : 3-dihydrothionaphthen (IX), respectively, when heated at 270° without a solvent (see Schemes C and D, respectively).

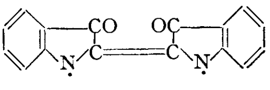




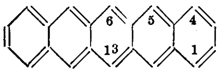
Disproportionation Reactions of Biradicals.—The orange dehydroindigo breaks down at 195° into indigo on the one hand and higher oxidation products on the other (Kalb, *Ber.*, 1909, **42**, 3643). This behaviour cannot be forecast from the classical structural formula, but is in agreement with the radical formula (X) and recalls the formation of diphenylamine (see B).

The question whether dehydroindigo has a diamagnetic biradical structure or a paramagnetic one is left open. The former structure is one of the canonical structures among which the " normal " molecule resonates (see Szwarc, Faraday Society Discussion, 1947, No. 2, p. 78).

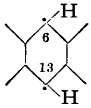
The term " biradical," introduced by the senior author (Schönberg and Vargha, *Annalen*, 1930, **483**, 179), may be defined as follows : " Biradicals are coloured substances which are similar in their chemical reactions to the triarylmethyl, diarylnitrogen, etc., radicals. They possess two centres of enhanced reactivity and are thermolabile. Their chemical behaviour cannot be expressed by structural formulæ based on the rules of classical organic chemistry."



(X.)



(XI.)



(XI*a*.)

This definition—in contradistinction to a definition based on the magnetic properties of compounds—allows the grouping under one heading of substances which are similar in their chemical reactions. For instance, dehydroindigo may be grouped with the violet pentacene, for which (XI) is the generally accepted formula. But pentacene undergoes disproportionation at 300° with the formation of 6 : 13-dihydropentacene (Clar, " Aromatische Kohlenwasserstoffe," p. 182, Berlin, 1941). Its formation recalls the synthesis of triphenylmethane when triphenylmethyl is heated (Wieland and Müller, *Annalen*, 1913, **401**, 235), and is in agreement with (XI*a*) (abbreviated formula for pentacene) but not with (XI).

EXPERIMENTAL.

Thermal Decomposition of Diphenyl Disulphide.—The pyrolysis was carried out in an apparatus similar to that employed for vacuum distillation (using a Liebig condenser) but without a capillary tube; the receiver was immersed in ice–salt. The pyrolysis flask (*A*) was in the form of a test-tube with a side tube; (*A*) was sealed after introduction of diphenyl disulphide (5·5 g.) and passage through it of a dry stream of carbon dioxide to replace the air. During pyrolysis (bath temp. 270°; 6 hours), the apparatus was connected to a water-pump. Drops were formed in the receiver, the smell of thiophenol was noticed, and the colour reaction with sodium nitrite in the presence of glacial acetic acid was obtained (Rheinboldt, *Ber.*, 1927, **60**, 184). Pyrolysis was thus carried out under conditions which allow thiophenol to escape as soon as formed. The drops collected were treated with benzoyl chloride in the presence of aqueous sodium hydroxide, and colourless crystals were obtained which, after recrystallisation from ethyl alcohol, were proved to be phenyl thiobenzoate (m. p. and mixed m. p.) (Found : C, 72·6; H, 4·9; S, 14·9. Calc. for $C_{13}H_{10}OS$: C, 72·9; H, 4·7; S, 14·9%). The yield was about 33% (after crystallisation), but the amount of thiophenol produced is higher than that calculated from the amount of ester obtained, as the benzoylation is not quantitative. (Diphenyl disulphide was unaffected by benzoyl chloride under the same conditions.) The contents of (*A*) * were allowed to cool and a small quantity of alcohol was added. After standing at 0° overnight, colourless crystals were obtained and recrystallised from alcohol; they were proved by m. p. and mixed m. p. and the colour reaction with concentrated sulphuric acid to be thianthren (I); yield about 60% (Found: C, 66·5; H, 4·0; S, 29·2. Calc. for $C_{12}H_8S_2$: C, 66·7; H, 3·7; S, 29·6%).

Thermal Decomposition of pp′-*Ditolyl Disulphide.*—Similar thermal decomposition of this disulphide afforded thio-*p*-cresol (identified by m. p. and mixed m. p.).

Pyrolysis of αβ-Bisphenylthiostilbene (IIa).—This stilbene (3 g.) (Posner, *loc. cit.*) was subjected to pyrolysis as described above, and the formation of thiophenol was established in the same way. The contents of the pyrolysis flask were extracted several times with light petroleum (b. p. 30—50°) and on slow evaporation gave colourless crystals of tolan (m. p. and mixed m. p.).

*Preparation of αβ-Bis-*p*-tolylthiostilbene* (IIb).—Benzoin (5 g.) was dissolved in the minimal amount of glacial acetic acid, and treated with thio-*p*-cresol (7·8 g.). The reaction mixture was saturated with dry hydrogen chloride and sticks of anhydrous zinc chloride (cf. Posner, *loc. cit.*) were added. The mixture was kept overnight in an ice-chest, and colourless crystals separated; they were filtered off, washed with cold ethyl alcohol and with light petroleum (b. p. 30—50°), and crystallised from hot benzene; m. p. 170° (Found: C, 78·9; H, 5·5; S, 15·0. $C_{28}H_{24}S_2$ requires C, 79·2; H, 5·7; S, 15·1%). The *stilbene* was difficultly soluble in hot ethyl alcohol and light petroleum (b. p. 70—80°) and soluble in hot benzene. On pyrolysis as above, it gave thio-*p*-cresol (m. p. and mixed m. p.).

Preparation of αβ-Bisphenylthio-αβ-dicumylethylene (IIc).—Couminoin (5 g.) (Feigland *et al.*, *Ber.*, 1925, **58**, 2300), dissolved in the minimal amount of glacial acetic acid, was treated with thiophenol (5 g.) in the presence of dry hydrogen chloride, as described above. The crystals of the *ethylene* that separated from the mother-liquor (M) were filtered off, washed with light petroleum (b. p. 70—80°), and recrystallised from benzene; m. p. 182° (Found: C, 80·0; H, 6·7; S, 13·0. $C_{32}H_{32}S_2$ requires C, 80·0; H, 6·7; S, 13·3%). It was soluble in hot benzene and toluene and difficultly soluble in cold ethyl alcohol and light petroleum (b. p. 70—80°). On pyrolysis, (II*c*) gave thiophenol (identified as phenyl thiobenzoate). The mother-liquor (M) was poured into water, and the mixture extracted with ether; the extract was washed with dilute aqueous sodium hydroxide solution then with water, and dried (Na_2SO_4). After evaporation of the ether, recrystallisation from hot benzene afforded more of the product.

Thermal Decomposition of 2 : 2′-*Diketo*-3 : 3′-*diphenyl*-3 : 3′-*dicoumaranyl* (VI).—This compound (1 g.) (Schönberg and Mustafa, *J.*, 1945, 660) was heated in a test-tube (*A*) connected by a bent tube to a similar tube (*B*) externally cooled by ice–salt. Facilities were provided to allow a stream of dry carbon dioxide to pass through the apparatus when air was displaced; then pyrolysis (bath temp. 270°) was carried out for ½ hour. Colourless crystals appeared on the walls of (*A*) and (*B*). They were collected, and recrystallised from benzene–light petroleum (b. p. 30—50°) in colourless crystals, m. p. 114°, proved to be the lactone of *o*-hydroxydiphenylacetic acid (VII) by m. p., mixed m. p., and colour reaction with sulphuric acid (Bistrzycki and Flatau, *Ber.*, 1895, **28**, 989).

Pyrolysis of 2 : 2′-*Diphenylthioindigo-white* (VIII).—This substance (0·5 g.) (Schönberg and Mustafa, *loc. cit.*) was subjected to pyrolysis as described for (VI). On the walls of tube (*A*), oily drops appeared which solidified on cooling. The solid crystallised from ethyl alcohol in colourless crystals, m. p. 105°, proved to be 3-keto-2-phenyl-2 : 3-dihydrothionaphthen (IX) by m. p., mixed m. p., and the colour reaction with sulphuric acid (Kalb and Baeyer, *loc. cit.*).

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