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THE FORMATION OF STILBENES AND PHENANTHRENES BY IRRADIATION OF DIBENZYL SULFIDES

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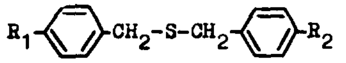
Carruthers' (1) recent paper has urged us to present a preliminary account of a part of our investigations on the photochemistry of organic compounds.

By column chromatography of reaction mixtures, obtained by UV irradiation of $0.5-1\cdot 10^{-2}$ molar solutions of dibenzyl sulfide (Ia) in hexane



I_a: $R_1 = R_2 = H$
I_b: $R_1 = R_2 = CH_3$
I_c: $R_1 = H$; $R_2 = CH_3$

we isolated in accordance with Carruthers: benzyl mercaptane (II), bibenzyl (III), trans-stilbene (IV), phenanthrene (V) and dibenzyl disulfide (VI). In addition a new compound was isolated which turned out to be α,α-bis(benzylthio)toluene, $C_6H_5CH(SCH_2C_6H_5)_2$ (VII). Furthermore UV spectrophotometry showed that toluene was also present.

When Ia was irradiated in methanolic or ethanolic solution or in acetic acid the same compounds were found but there was also some hydrogen sulfide present.

Using gas-liquid chromatography an attempt was made to establish the sequence in which the compounds appear in the reaction mixture.

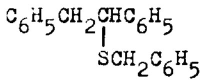
After two hours of irradiation only bibenzyl, benzylmercaptane and dibenzyl disulfide were found. After four hours small amounts of stilbene and phenanthrene could also be detected. If the irradiation was continued until the starting product had disappeared (16 hours), the amounts of stilbene and phenanthrene had increased whereas the relative amounts of the sulfur containing substances, mercaptane and disulfide, had diminished. Besides the peaks of these principal products, several minor peaks of other compounds appeared in the chromatogram of the last experiment.

Similar observations were made on the irradiation mixture of 4,4'-dimethyl dibenzyl sulfide (Ib).

From irradiation experiments with the unsymmetrically substituted derivative Ic it was clear that the stilbenes and phenanthrenes have to arise via compounds formed earlier from break-down products of the starting component. Under the influence of light Ic gave, as well as the monomethyl derivatives of III, IV and V, also the corresponding non substituted and symmetrical disubstituted compounds. The proportions of related products in this case were almost the same as those obtained from UV photolysis of an equimolecular mixture of Ia and Ib. So, stilbene cannot be the product of some intramolecular transformation of dibenzyl sulfide.

No 4-methylstilbene or 3-methylphenanthrene could be detected among the irradiation products of a mixture of Ia and 4-methylbibenzyl and only a trace of unsubstituted phenanthrene was formed photochemically from a mixture of Ib and bibenzyl. From these results it was concluded that bibenzyl could not be an important intermediate in the formation of stilbenes.

Another possible precursor of stilbenes in our experiments seemed to be 1,2-diphenylethyl benzyl sulfide (VIII),



$$C_6H_5CH_2\underset{SCH_2C_6H_5}{\underset{|}{C}}HC_6H_5$$

(VIII)

It could easily be formed by photolysis of dibenzyl sulfide and might be a source of bibenzyl radicals which then could disproportionate to stilbene and bibenzyl. Photolysis of VIII resulted in a similar mixture as that obtained from I but the relative proportions of the various reaction products differed greatly. After only two hours of irradiation the main products were bibenzyl and phenanthrene which appeared in about equal amounts. Compound VII was also found and benzyl mercaptane and dibenzyl disulfide were present only in small quantities. After irradiation for five hours the starting compound had disappeared but the composition of the reaction mixture was nearly the same as with shorter irradiation times. All peaks present in the gas chromatogram of these irradiation products were also observed in the G.L.chromatogram of the irradiated products of I. In accordance with these results the main products in irradiation of 1-tolyl-2-phenylethyl benzyl sulfide, $4\text{-}CH_3C_6H_4\underset{SCH_2C_6H_5}{\underset{|}{C}}HCH_2C_6H_5$, were p.methylbibenzyl and 3-methylphenanthrene. Unsubstituted bibenzyl, stilbene, phenanthrene and dibenzyl sulfide were minor products in this case. From these results it seems probable that the formation of stilbenes and phenanthrene, unexplained in the paper of Carruthers, takes place via compound VIII.

As several not too unstable radicals seem to arise from the photolysis of dibenzyl sulfides it is rather difficult to present a complete series of reaction steps which may describe the formation of the various products isolated. A tentative scheme may be, however, as follows.

UV irradiation of dibenzyl sulfide splits the molecule into benzyl and benzylthiyl radical (a),

(a) $\Phi CH_2SCH_2\Phi \xrightarrow{h\nu} \Phi CH_2\cdot + \Phi CH_2S\cdot$

These give rise to a third radical, $C_6H_5CH_2S\dot{C}HC_6H_5$ (IX) by hydrogen removal from the starting compound, thus explaining the presence of toluene and benzylthiol in the reaction mixture (b and c),

(b) $\Phi CH_2\cdot + \Phi CH_2SCH_2\Phi \rightarrow \Phi CH_3 + \Phi CH_2S\dot{C}H\Phi$ (IX)

(c) $\Phi CH_2S\cdot + \Phi CH_2SCH_2\Phi \rightarrow \Phi CH_2SH + \Phi CH_2S\dot{C}H\Phi$ (IX)

Bibenzyl and dibenzyl disulfide are formed by dimerization of benzyl and benzylthiyl radicals (d and e) or by reactions of these radicals with unchanged dibenzyl sulfide (f and g),

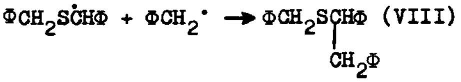
(d) $2\ \Phi CH_2\cdot \rightarrow \Phi CH_2CH_2\Phi$ (III)

(e) $2\ \Phi CH_2S\cdot \rightarrow \Phi CH_2SSCH_2\Phi$ (VI)

(f) $\Phi CH_2\cdot + \Phi CH_2SCH_2\Phi \rightarrow \Phi CH_2CH_2\Phi$ (III) $+ \Phi CH_2S\cdot$

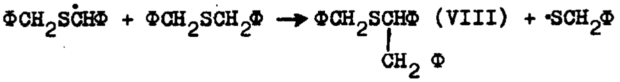
(g) $\Phi CH_2S\cdot + \Phi CH_2SCH_2\Phi \rightarrow \Phi CH_2SSCH_2\Phi$ (VI) $+ \Phi CH_2\cdot$

Also in an analogous manner the radical IX may combine with benzyl or benzylthiyl radicals (h and i) or eventually may interact with the starting compound giving rise to the formation of compounds VII and VIII (j and k),

(h) 

$\Phi CH_2S\dot{C}H\Phi + \Phi CH_2\cdot \rightarrow \Phi CH_2S\underset{\displaystyle CH_2\Phi}{\underset{|}{C}}H\Phi$ (VIII)

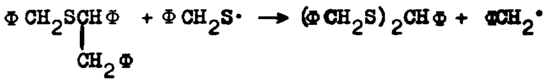
(i) $\Phi CH_2S\dot{C}H\Phi + \cdot SCH_2\Phi \rightarrow (\Phi CH_2S)_2CH\Phi$ (VII)

(j) 

$\Phi CH_2S\dot{C}H\Phi + \Phi CH_2SCH_2\Phi \rightarrow \Phi CH_2S\underset{\displaystyle CH_2\Phi}{\underset{|}{C}}H\Phi$ (VIII) $+ \cdot SCH_2\Phi$

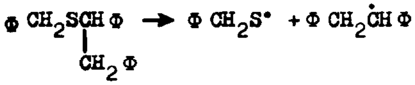
(k) $\Phi CH_2S\dot{C}H\Phi + \Phi CH_2SCH_2\Phi \rightarrow (\Phi CH_2S)_2CH\Phi$ (VII) $+ \cdot CH_2\Phi$

As many benzyl and benzylthiyl radicals disappear from the solution by dimerization or reaction with the solvent, then in the photolysis of dibenzyl sulfide the concentration of $C_6H_5CH_2S\dot{C}HC_6H_5$ radicals which arise only via the former radicals will be low and so the products VII and VIII will be present in only small amounts. However, by irradiation of VIII $C_6H_5CH_2S\dot{C}HC_6H_5$ will be formed in the first step and now VII will appear in higher amounts, e.g. as formuled in (1),

(1) 

$$\Phi CH_2S\underset{CH_2\Phi}{CH}\Phi + \Phi CH_2S\cdot \rightarrow (\Phi CH_2S)_2CH\Phi + \Phi CH_2{}^{\bullet}$$

The stilbenes (and phenanthrene) seem to arise only via VIII, possibly by disproportionation of primarily formed bibenzyl radicals (m and n),

(m) 

$$\Phi CH_2S\underset{CH_2\Phi}{CH}\Phi \rightarrow \Phi CH_2S^{\bullet} + \Phi CH_2\dot{C}H\Phi$$

(n) $2\Phi CH_2\dot{C}H\Phi \rightarrow \Phi CH{=}CH\Phi + \Phi CH_2CH_2\Phi$

The disulfide (VI) might be the oxidizing agent in the oxidation of dihydrophenanthrene formed from irradiation of stilbene.

$$\Phi CH{=}CH\Phi\,(cis) \xrightarrow{h\nu} \text{phenanthrene.}$$

A more extended survey of this work will be published elsewhere.

(1) W.Carruthers, Nature, 209, 908 (1966).