

### 347. Photochemical Changes of Some Deoxybenzoins.

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In absence of air, deoxybenzoin undergoes photolysis to dibenzyl, benzaldehyde, didesyl, and an amorphous solid, by a free-radical mechanism. The existence of benzaldehyde is explicable if benzoyl radicals dehydrogenate deoxybenzoin to free desyl radicals. Some deoxybenzoins substituted in the aryl and the methylene group undergo analogous photolyses.

In air and light, deoxybenzoin and its 4 : 4'-disubstituted derivatives are oxidised to aldehydic and acidic products, probably *via* a hydroperoxide. Methylene-substituted deoxybenzoins resist such photolysis.

So far as we are aware, little is known regarding the photolysis of deoxybenzoins (I). Paterno, Chieffi, and Perret<sup>1</sup> and Cohen,<sup>2</sup> however, obtained a deoxybenzoinpinacol,



benzoic acid, and a resin when deoxybenzoin was irradiated in presence of toluene or ethanol. In the light of this and of our observation that deoxybenzoin undergoes an obvious change on exposure to air and light, the photolysis of this ketone and ten of its derivatives has been systematically studied.

The deoxybenzoins were chosen with a view to determining the influence of the substituent groups on the susceptibility of the ketones to photochemical changes, the substituents (X, X') in the phenyl groups being methoxy or nitro, and those (R) on the

<sup>1</sup> Paternò, Chieffi, and Perret, *Gazzetta*, 1914, **44**, I, 151.

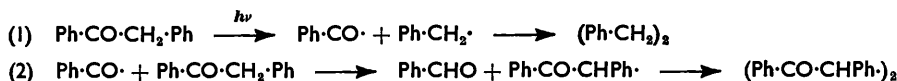
<sup>2</sup> Cohen, *Chem. Weekblad*, 1916, **13**, 902.

methylene group being methyl, ethyl, phenyl, or diphenyl, and, of course, deoxybenzoin itself. These were irradiated in benzene in the absence and in the presence of air, and in certain cases pyridine was added to enhance enolisation.

*Photolysis in Absence of Air.*—Irradiation of deoxybenzoin in an atmosphere of carbon dioxide under the conditions specified in the Experimental section led to the formation of dibenzyl, didesyl, benzaldehyde, and an amorphous product. However, the isolation of these photolysis products from unchanged deoxybenzoin was difficult and caused formation of traces of benzoic acid.

On the other hand, irradiation of deoxybenzoins substituted in an aryl group (4-methoxy-, 4:4'-dimethoxy-, 4'-nitro-, 4-methoxy-4'-nitro-deoxybenzoin) did not effect substantial degradation, though traces of *p*-anisaldehyde and a resin were obtained from the first member.

The results support the annexed reaction scheme, in which the benzaldehyde results from the reaction between a benzoyl radical and a deoxybenzoin molecule.



Unlike those substituted in the aryl group, deoxybenzoins substituted in the methylene group undergo profound change. The results so far obtained are in agreement with the mechanism proposed. This may be exemplified by the photolysis of the deoxybenzoin (I; X = X' = H, R = Me) to benzaldehyde, *meso*- and ( $\pm$ )-2:3-diphenylbutane, and an amorphous solid, which requires rupture of the excited molecule to free benzoyl, 1-phenyl-

TABLE I.

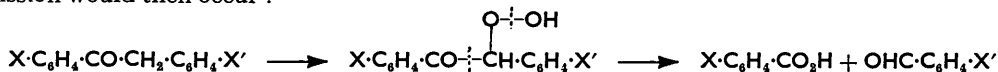
Deoxybenzoin (I)			Aldehyde	Dibenzyl
X	X'	R		
H	H	H	Ph·CHO	Dibenzyl
H	H	Me	"	<i>meso</i> - and ( $\pm$ )-2:3-Diphenylbutane
H	H	Et	"	<i>meso</i> -3:4-Diphenylhexane
OMe	OMe	Me	<i>p</i> -MeO·C <sub>6</sub> H <sub>4</sub> ·CHO	<i>meso</i> - and ( $\pm$ )-2:3-Di-( <i>p</i> -methoxyphenyl)butane
OMe	OMe	Et	"	<i>meso</i> -Hexaestrol dimethyl ether
H	H	Ph	Ph·CHO"	<i>sym</i> -Tetraphenylethane

ethyl,  $\alpha$ -methyldesyl, and hydrogen radicals. Nevertheless, experimental evidence for the existence of  $\alpha$ -methyldesyl radicals is lacking since di- $\alpha$ -methyldesyl could not be separated.

Likewise, three ethyl-substituted deoxybenzoins gave the corresponding aldehydes and dibenzyls (which possess oestrogenic activity). Contrary to Schönberg and Mostafa,<sup>3</sup> the derivative (I; X = X' = H, R = Ph) is susceptible to irradiation, giving benzaldehyde, *sym*-tetraphenylethane, and an amorphous solid. The diphenyl derivative, however, failed to undergo a change, in agreement with Banchetti's observation.<sup>4</sup>

*Photolysis in Presence of Air.*—When the above-mentioned deoxybenzoins were irradiated in contact with dry air most of the degradation products obtained by irradiation in the absence of air were isolated, together with acidic and aldehydic degradation products. For example, deoxybenzoin gave benzaldehyde and benzoic acid in appreciable quantities, and peroxides were also detected; dibenzyl and didesyl were not isolated. Similarly, deoxybenzoins substituted in the aryl group gave, in air, the appropriate substituted benzoic acids and benzaldehydes.

There is evidence that ketones are autoxidised in the  $\alpha$ -position to hydroperoxides, and fission would then occur:



On the other hand, as has been shown above, photolysis in the absence of air gives rise to the isomeric aldehyde X·C<sub>6</sub>H<sub>4</sub>·CHO: if both these reactions occur concurrently then,

<sup>3</sup> Schönberg and Mostafa, *J.*, 1945, 659.

<sup>4</sup> Banchetti, *Gazzetta*, 1941, 71, 685.

when  $X = \text{OMe}$  and  $X' = \text{H}$ , the products of the combined reactions would be benzoic and *p*-anisic acid, and benzaldehyde and *p*-anisaldehyde, which is what is found.

Photolysis of 2-chlorodeoxybenzoin, involving peroxide formation, was studied by Jenkins<sup>5</sup> who obtained *o*-chlorobenzoic acid and benzaldehyde arising from *o*-chlorobenzoyl and benzyl residues. On the contrary, photolysis of the methylene-substituted deoxybenzoin did not seem to involve autoxidation since peroxides could not be detected and lower aromatic ketones were not isolated. This may be because, in some cases, the mobility of the hydrogen atom attached to tertiary carbon ( $\text{>CH-}$ ), necessary for peroxide formation, is restricted. Nevertheless, the aldehydes and substituted dibenzyls isolated may be attributed to photolysis.

In most of the photolyses, amorphous products were amongst those isolated. Analyses of some of these did not identify them as polydidesyls or polydeoxybenzoin. The identity of the substituted dibenzyls was established by analysis and by comparison with authentic specimens prepared by the hydrogenation of the corresponding ketazines.<sup>6</sup>

#### EXPERIMENTAL

The light petroleum used had b. p. 60–80°. All reagents were purified before use.

*Method.*—Portions (2 g.) of the anhydrous deoxybenzoin in benzene (100 ml.) were placed in four series of Pyrex photochemical tubes, of which two were sealed in an atmosphere of carbon dioxide with, and without, pyridine (10 ml. per tube) severally. The other two series, one with, and one without, pyridine were irradiated in contact with dry air. The specimens were exposed to sunlight in Alexandria, Egypt, for 30 days during March–June. A control sample for each of the four series was kept in the dark and no change in them was perceptible.

The peroxides found in some of the aerated samples were detected by the method described by Green and Schoetzow.<sup>7</sup>

*Estimation of acidic and aldehydic components.* The photolysed deoxybenzoin solutions were diluted with ether or benzene, shaken with saturated sodium hydrogen carbonate solution (3 × 20 ml.), and washed with water (2 × 20 ml.). To the combined sodium hydrogen carbonate extracts and water washings, 2*N*-hydrochloric acid (150 ml.) was added. The acid mixture was extracted with ether (2 × 100 ml.), and the extract washed with ice-cold water (3 × 20 ml.). The acid residue recovered from the ether was weighed, dissolved in 50% neutral ethanol (*ca.* 50 ml.), and titrated against 0.05*N*-sodium hydroxide (phenolphthalein), whence the amounts of the acids were determined. In the case of the unsymmetrically substituted deoxybenzoin the percentage weights of the mixed acids were derived by calculation; the component acids were separated by fractional crystallisation, and their identities were confirmed by mixed m. p. determinations.

When pyridine was present in the irradiated solution the method of isolation was as follows: The irradiated solutions were diluted with ether or benzene and washed with water (2 × 50 ml.), 2*N*-hydrochloric acid (3 × 50 ml.), water, and finally sodium hydrogen carbonate solution. To all the washings, combined, 2*N*-hydrochloric acid was added and the acidic degradation products were extracted with ether and estimated as before.

For estimation of aldehydic products, the residual acid-free solution was shaken with freshly prepared sodium hydrogen sulphite solution (75 ml.). The aqueous bisulphite layer, together with water-washings (2 × 20 ml.) of the organic layer, was mixed with an equal volume of saturated sodium carbonate solution and steam-distilled into dimedone or 2:4-dinitrophenylhydrazine reagent. After being kept overnight in the ice-chest, the aldehydic derivative was collected, washed, dried, and weighed.

The mean results of these determinations are recorded in Table 2. They are derived from at least four replicates. For the unsymmetrically substituted deoxybenzoin the weights of the 2:4-dinitrophenylhydrazones of the volatile aldehydes isolated are recorded; in other cases, the aldehydes were only identified.

After separation of the acidic and aldehydic components of the irradiated solutions, the other photolysis products were isolated from the neutral benzene solutions as described below.

*Deoxybenzoin.* The benzene solution (from 5 × 2 g. portions) was evaporated and the brown viscous residue was extracted with cold light petroleum. The insoluble resinous residue was purified by dissolution in benzene and precipitation with light petroleum. This process

<sup>5</sup> Jenkins, *J. Amer. Chem. Soc.*, 1935, **57**, 2733.

<sup>6</sup> Bretschneider and Ajtai, *Ber.*, 1941, **74**, 571; Fodor *et al.*, *Ber.*, 1941, **74**, 589; *J.*, 1948, 684.

<sup>7</sup> Green and Schoetzow, *J. Amer. Pharm. Assoc.*, 1933, **22**, 412.

TABLE 2. Irradiation products ( $Y = p\text{-X}\cdot\text{C}_6\text{H}_4\text{-}$ ;  $Y' = p\text{-X}'\cdot\text{C}_6\text{H}_4\text{-}$ ).

Subst.			Irradn. in :							
			$\text{CO}_2$		$\text{CO}_2\text{-C}_5\text{H}_5\text{N}$		Air		Air-C <sub>5</sub> H <sub>5</sub> N	
X	X'	R	Y-CHO	Y'-CO <sub>2</sub> H	Y-CHO	Y'-CO <sub>2</sub> H	Ar-CHO	Ar-CO <sub>2</sub> H	Ar-CHO	Ar-CO <sub>2</sub> H
H	H	H	3.24	0.69	1.52	1.24	2.25	18.14	1.72	33.23
OMe	H	H	1.27	0.20	1.75	0.64	4.20	4.92	2.80	14.98
OMe	OMe	H	3.73	0.68	0.34	3.43	3.00	19.72	1.99	40.05
H	NO <sub>2</sub>	H	0.09	0.47	0.05	0.64	—	0.50	—	33.40
OMe	NO <sub>2</sub>	H	0.09	0.52	0.06	0.88	—	1.50	—	36.95
H	H	Me	12.39	0.80	—	—	3.44	24.00	—	—
H	H	Et	11.38	0.72	—	—	3.44	21.77	—	—
OMe	OMe	Me	8.96	0.81	—	—	3.62	16.95	—	—
OMe	OMe	Et	7.93	0.85	—	—	3.71	15.20	—	—
H	H	Ph	9.59	0.79	—	—	2.60	18.68	—	—

was repeated several times until the resinous material was obtained as a yellowish-white amorphous powder (0.75 g.), m. p. 167—175° (decomp.) [Found : C, 85.4, 85.2; H, 5.6, 5.7. Calc. for  $(\text{C}_{14}\text{H}_{11}\text{O})_n$  : C, 86.1; H, 5.6. Calc. for  $(\text{C}_{14}\text{H}_{12}\text{O})_n$  : C, 85.7; H, 6.1%].

The light petroleum extract was evaporated at room temperature, yielding unchanged crystalline deoxybenzoin (7.5 g.) and an oil. The latter (1.59 g.) was further purified by treatment with cold light petroleum in which it is more soluble than deoxybenzoin. The oil gave, on distillation fractions (a) (0.4 g.) b. p. <120°/1.2 mm. and (b) b. p. 120—150°/1.2 mm. The former yielded dibenzyl which crystallised from ethanol in prismatic needles,<sup>8</sup> m. p. and mixed m. p. 52°.

Didesyl (0.1 g.) separated from the deoxybenzoin fraction on treatment with ice-cold ether in which it is sparingly soluble. It crystallised from benzene-light petroleum in prismatic needles,<sup>9</sup> m. p. and mixed m. p. 245° (Found : C, 86.1; H, 5.5. Calc. for  $\text{C}_{28}\text{H}_{22}\text{O}_2$  : C, 86.1; H, 5.6%), which gave a grass-green colour with concentrated sulphuric acid.<sup>10</sup>

The deoxybenzoin solutions which were irradiated in presence of air gave a positive peroxide test and did not yield dibenzyl or didesyl.

4-Methoxydeoxybenzoin,<sup>11</sup> 4 : 4'-dimethoxydeoxybenzoin,<sup>12</sup> 4'-nitrodeoxybenzoin,<sup>13</sup> and 4-methoxy-4'-nitrodeoxybenzoin<sup>14</sup> did not give photolysis products other than the aldehydes and acids recorded in the Table.

$\alpha$ -Phenylpropiofenone (I; X = X' = H, R = Me).<sup>15</sup> The benzene solution (from 6 × 2 g. portions) left after separation of benzoic acid and benzaldehyde yielded a pale brown viscous residue which was extracted with cold light petroleum. The oil (3.5 g.) recovered from this extract was treated with ice-cold methanol, and the solution gave *meso*-2 : 3-diphenylbutane (0.9 g.) on slow evaporation. It crystallised from methanol in flakes,<sup>16</sup> m. p. and mixed m. p. 126° (Found : C, 91.1; H, 8.7. Calc. for  $\text{C}_{16}\text{H}_{18}$  : C, 91.4; H, 8.6%). (More *meso*-2 : 3-diphenylbutane was obtained as a sublimate when the residual oil was heated with traces of iodine for 6 hr. at 230—240°; under these conditions the oily 2 : 3-diphenylbutane, likely to be present, is converted into the racemic isomeride.<sup>17</sup>) The brown resinous residue which was insoluble in light petroleum was purified by treatment with benzene-light petroleum as before, yielding an amorphous solid, m. p. 163° (decomp.) (Found : C, 83.4; H, 6.0, 5.9%).

$\alpha$ -Phenylbutyrophenone.<sup>15</sup> The brown viscous residue recovered from the benzene solution was extracted with cold light petroleum. On slow evaporation the extract gave an odorous oil in about 30% yield with respect to the deoxybenzoin. It gave on distillation a fraction, b. p. 158—160°/1.2 mm., which did not solidify. *meso*-3 : 4-Diphenylhexane was obtained from the first fraction after the oily impurities had been removed with cold methanol. It crystallised from methanol in needles,<sup>18</sup> m. p. and mixed m. p. 91—92° (Found : C, 90.5; H, 9.35. Calc. for  $\text{C}_{18}\text{H}_{22}$  : C, 90.75; H, 9.25%).

<sup>8</sup> Alexander and Fuson, *J. Amer. Chem. Soc.*, 1936, **58**, 1745.

<sup>9</sup> Knoevenagel, *Ber.*, 1888, **21**, 1355.

<sup>10</sup> Fehrlin, *Ber.*, 1889, **22**, 553; Hahn and Murray, *J. Amer. Chem. Soc.*, 1914, **36**, 1489.

<sup>11</sup> Ney, *Ber.*, 1888, **21**, 2450.

<sup>12</sup> Stobbe, *Ber.*, 1902, **35**, 912.

<sup>13</sup> Petrenko-Kritschenko, *Ber.*, 1892, **25**, 2242.

<sup>14</sup> Rubin and Wishinsky, *J. Amer. Chem. Soc.*, 1944, **66**, 1948.

<sup>15</sup> Meyer and Oelker, *Ber.*, 1888, **21**, 1297.

<sup>16</sup> Haword, Hilbert, Wiebe, and Gaddy, *J. Amer. Chem. Soc.*, 1932, **54**, 3639.

<sup>17</sup> Lyepin, *J. Russ. Phys. Chem. Soc.*, 1912, **44**, 1190.

<sup>18</sup> Fodor and Wein, *J.*, 1948, 686.

*p*-Methoxy- $\alpha$ -*p*'-methoxyphenylpropiofenone.<sup>19</sup> The neutral aldehyde-free residue recovered from the benzene solution (from  $5 \times 2$  g. portions) was extracted with cold light petroleum. When this extract was evaporated at room temperature, an oil contaminated with *meso*-2 : 3-di-(*p*-methoxyphenyl)butane was obtained. On treatment with ice-cold methanol, the oil dissolved, leaving crystalline *meso*-2 : 3-di-(*p*-methoxyphenyl)butane (0.8 g.). It recrystallised from methanol in prismatic needles,<sup>20</sup> m. p. 136° (Found : C, 79.5; H, 8.2. Calc. for  $C_{18}H_{22}O_2$  : C, 80.0; H, 8.2%). Racemic 2 : 3-di-(*p*-methoxyphenyl)butane was obtained from the methanolic solution of the oil, after separation of the *meso*-isomer, by dilution with water and extraction with ether. The residue which was recovered from the ethereal solution was dissolved in a minimum of ethanol and kept in the ice-chest; the racemic compound crystallised. It separated from methanol in flakes<sup>20</sup> (0.2 g.), m. p. 87° (Found : C, 79.6; H, 8.1%).

*p*-Methoxy- $\alpha$ -*p*'-methoxyphenylbutyrophenone.<sup>19</sup> The neutral anisaldehyde-free residue (from  $9 \times 2$  g. portions), which was obtained as a pale brown viscous oil, was extracted with light petroleum, and the solution evaporated at room temperature. The oily residue (4.6 g.) which was contaminated with minute crystals was treated with ice-cold methanol in which the oil dissolved leaving *meso*-hexestrol dimethyl ether (1.8 g.). This separated from methanol in prisms,<sup>21</sup> m. p. and mixed m. p. 144° (Found : C, 80.4; H, 8.8. Calc. for  $C_{20}H_{26}O_2$  : C, 80.5; H, 8.7%).

*meso*- $\alpha\alpha$ -Diphenylacetophenone.<sup>22</sup> The benzaldehyde-free neutral benzene solution was concentrated and then carefully diluted with light petroleum; *sym*-tetraphenylethane separated in about 25% yield with respect to the original ketone. It crystallised from benzene-light petroleum in prisms,<sup>23</sup> m. p. and mixed m. p. 211° (Found : C, 93.3; H, 6.7. Calc. for  $C_{26}H_{22}$  : C, 93.4; H, 6.6%).

No photolysis products were obtained from *meso*- $\alpha\alpha\alpha$ -triphenylacetophenone and all the methylene-substituted deoxybenzoinis irradiated in contact with dry air gave negative peroxide tests.

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[Received, November 4th, 1955.]

<sup>19</sup> Dodds and Goldberg, *Proc. Roy. Soc.*, 1939, **B**, 127, 140.

<sup>20</sup> Wessely, Bauer, Chwala, Plaichinger, and Schönbeck, *Monatsh.*, 1948, **79**, 596.

<sup>21</sup> Ajtai, *Ber.*, 1941, **74**, 582; Dodds, Goldberg, and Grunfeld, *Proc. Roy. Soc.*, 1944, **B**, 132, 83.

<sup>22</sup> Koelsch, *J. Amer. Chem. Soc.*, 1932, **54**, 2051.

<sup>23</sup> Norris, Thomas, and Brown, *Ber.*, 1910, **43**, 2959.