LXVII.—*p-Desylphenol.*

By FRANCIS R. JAPP, F.R.S., and G. H. WADSWORTH, Associate of the Normal School of Science.

100 grams of benzoïn and 150 grams of phenol were melted together, cooled, and gradually poured, while still liquid, into 1500 grams of concentrated sulphuric acid, stirring all the time. The temperature rose, and the solution assumed a dark reddish-brown colour. After standing over night, the mixture was poured, in a thin stream, into four times its bulk of cold water. A white substance, which proved to be a sulphonic acid, separated; part of this went into solution in the warm liquid, but was deposited on cooling, and the whole precipitate was thus obtained in a crystalline form, in which it could be readily filtered off.

In the first experiments which we made, the sulphuric acid was carefully cooled during the addition of the benzoïn and phenol, and the mixture was afterwards poured upon pounded ice. This procedure, however, offers no advantages over the foregoing.

The white sulphonic acid was separated by filtration, freeing it as far as possible from adhering sulphuric acid by means of the filter-pump, but not washing it, as it is far more soluble in pure water than in dilute sulphuric acid. It was then made into a thick cream with strong hydrochloric acid, and heated in sealed tubes at 150° during from three to four hours. The hydrolysed compound separated as a dark-coloured, amorphous mass in the tubes. It was boiled with a solution of sodium carbonate, in which it first fused and afterwards solidified; then it was washed with water, dried, and dissolved in hot benzene. From this solution it was deposited, on long standing, in thick, crystalline crusts consisting of hard, warty aggregations of needles, containing benzene of crystallisation (*vide infra*). It was recrystallised twice from benzene, and finally, for analysis, from light petroleum, from which it separates in minute, colourless laminæ melting constantly at 133°. It crystallises from dilute alcohol in large, very thin plates. It is readily soluble in caustic alkalis, and is precipitated from the solution by carbon dioxide, showing that it contains a phenolic hydroxyl-group. Under a pressure of 45 mm., it boils without decomposition at 309—314°.

Analysis agreed with the formula $C_{20}H_{16}O_2$:—

	Substance.	CO_2.	H_2O.
I	0·2342	0·7149	0·1142
II	0·1939	0·5905	0·0987

	Calculated for $C_{20}H_{16}O_2$.		Found.	
			I.	II.
C_{20}	240	83·33	83·24	83·04
H_{16}	16	5·56	5·41	5·65
O_2	32	11·11	—	—
	288	100·00		

Dr. Klingemann had the kindness to determine the molecular weight of the compound by Raoult's method, using acetic acid as a solvent:—

				Mol. wt.	
Wt. subst.	Wt. solv.	$\frac{\text{Wt. subst.} \times 100}{\text{Wt. solv.}}$.	Depression.	Found.	Calc. for $C_{20}H_{16}O_2$.
0·3525	19·943	1·768	0·22°	313	288

(Molecular depression of acetic acid = 39.)

The crystals deposited from benzene have the formula $C_{20}H_{16}O_2,C_6H_6$.

It is difficult to air-dry them without efflorescence; hence only 20 per cent. of benzene was found, instead of the calculated 21·3 per cent.

In order to ascertain the composition of the sulphonic acid which is first formed, the calcium salt was prepared and analysed. For this purpose, the sulphonic acid, after filtering it from the dilute sulphuric acid as already described, was dissolved in hot sodium carbonate, from which solution a sparingly soluble sodium salt separated on cooling; this was purified by recrystallisation from boiling alcohol, which deposited it in tufts of lustrous, yellowish, flat needles or laminæ. In order to convert it into the calcium salt, it was dissolved in hot water, and the solution precpitated with calcium chloride. The calcium salt was washed with cold water, air-dried, and analysed. It is a crystalline, yellow powder, which dissolves sparingly in boiling water, and is re-deposited on cooling.

0·3870 gram, on heating at 140°, lost 0·0554 gram H_2O, and the resulting 0·3316 gram anhydrous salt, on ignition with sulphuric acid, gave 0·0582 gram $CaSO_4$.

	Calculated for $(C_{20}H_{15}O_2{\cdot}SO_3)_2Ca,7H_2O$.	Found.
H_2O in 100 parts	14·00	14·31

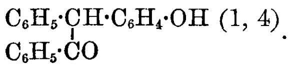
	Calculated for $(C_{20}H_{15}O_2{\cdot}SO_3)_2Ca$.	Found.
Ca in 100 parts	5·16	5·15

The compound $C_{20}H_{16}O_2$ is formed from benzoïn and phenol according to the equation

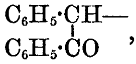
$$C_{14}H_{12}O_2 + C_6H_5{\cdot}OH = C_{20}H_{16}O_2 + H_2O,$$

the product being further converted into a sulphonic acid in the process.

A study of the reactions of the compound $C_{20}H_{16}O_2$ has led us to assign to it the constitution



$$\begin{array}{l} C_6H_5{\cdot}CH{\cdot}C_6H_4{\cdot}OH\ (1,\ 4) \\ \quad\ \ | \\ C_6H_5{\cdot}CO \end{array}.$$

Adopting the convenient name "desyl" which Victor Meyer has proposed for the radicle  $\begin{array}{l} C_6H_5{\cdot}CH— \\ C_6H_5{\cdot}CO \end{array}$, such a compound might be termed *p-desylphenol.*

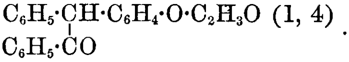
The elimination of water occurs between the hydroxyl-group of the benzoïn and the para-hydrogen-atom of the phenol, and the condensation thus resembles those of fatty alcohols with phenol described by Liebmann (*Ber.*, **14**, 1842), in which, however, zinc chloride was used as a dehydrating agent. We, therefore, tried to condense benzoïn and phenol with zinc chloride, so as to avoid the formation of the sulphonic acid, but without success.

Action of Acetic Anhydride.—*p*-Desylphenol was heated in a sealed tube with acetic anhydride for three hours at 150°; the excess of the anhydride was distilled off on the water-bath under reduced pressure, and the last traces destroyed by evaporation with alcohol. The product was twice recrystallised from light petroleum (b. p. 90—120°), from which it was deposited in slender, white needles melting at 106—107°. From alcohol, it crystallises in well-developed, oblique prisms. Under a pressure of about 40 mm., it distils without decomposition between 325° and 330°. Analysis showed that a monacetyl-derivative had been formed:—

	Substance.	CO_2.	H_2O.
I	0·2008	0·5894	0·0991
II	0·1540	0·4504	0·0765

	Calculated for $C_{22}H_{18}O_3$.		Found.	
			I.	II.
C_{22}........	264	80·00	80·04	79·76
H_{18}	18	5·45	5·48	5·52
O_3	48	14·55	—	—
	330	100·00		

Acetyl-p-desylphenol has the formula



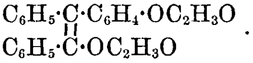
$$\begin{array}{l} C_6H_5\cdot CH\cdot C_6H_4\cdot O\cdot C_2H_3O \ (1,\ 4) \\ C_6H_5\cdot CO \end{array}$$

By heating *p*-desylphenol with acetic anhydride for three hours at 200°, a *diacetyl*-derivative is obtained. The compound was purified by recrystallisation from benzene, from which it is deposited in hemispherical aggregates of small, colourless needles melting constantly at 186—187°.

	Substance.	CO_2.	H_2O.
I........	0·2043	0·5793	0·1024
II........	0·2048	0·5811	0·1047

	Calculated for $C_{24}H_{20}O_4$.		Found.	
			I.	II.
C_{24}	288	77·41	77·33	77·38
H_{20}	20	5·37	5·56	5·68
O_4	64	17·22	—	—
	372	100·00		

The formation of a diacetyl-derivative can be accounted for on the assumption that at the high temperature of the reaction the group $CH\cdot CO$ of the *p*-desylphenol passes into the tautomeric tertiary form $C{:}C(OH)$, which is then acetylated. The compound would thus have the formula



$$\begin{array}{l} C_6H_5\cdot C\cdot C_6H_4\cdot OC_2H_3O \\ \qquad\ \ \| \\ C_6H_5\cdot C\cdot OC_2H_3O \end{array}.$$

Both the monacetyl- and the diacetyl-derivative, when boiled with caustic potash, regenerate *p*-desylphenol.

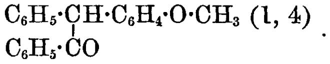
p-Desylanisoïl. — In methylating *p*-desylphenol, we employed a method introduced by Japp and Klingemann (Trans., 1888, 526) in the methylation of pyruvaldehydrazone. This method, which ensures complete alkylation, has since been used with good results by Victor Meyer, Beckmann, and others.

The desylphenol was dissolved in methyl alcohol with 4 molecular proportions of methyl iodide, and into this mixture, which was kept boiling in a flask fitted with a reflux condenser, a solution of four atomic proportions of sodium in methyl alcohol was gradually allowed to drop, so that the operation lasted about four hours. The greater part of the alcohol was then distilled off, caustic soda was added, so as to keep in solution any unchanged substance, if present, and the new compound was precipitated with water. The filtered alkaline solution gave no turbidity with hydrochloric acid, showing that the alkylation had been complete. The substance was distilled under reduced pressure, passing over between 292° and 298° under 43 mm. pressure. It was finally recrystallised three times from light petroleum, and formed colourless aggregates of flat needles melting at 90—92°. It is insoluble in caustic alkalis, showing that the methyl has replaced hydrogen of the phenolic hydroxyl. Analysis led to the formula $C_{21}H_{18}O_2$:—

	Substance.	CO_2.	H_2O.
I........	0·2141	0·6538	0·1158
II........	0·2181	0·6663	0·1174

	Calculated for $C_{21}H_{18}O_2$.		Found.	
			I.	II.
C_{21}	252	83·44	83·28	83·32
H_{18}	18	5·96	6·00	5·98
O_2	32	10·60	—	—
	302	100·00		

The compound is, therefore, *p-desylanisoïl*,



$$\begin{array}{l} C_6H_5\cdot \underset{|}{C}H\cdot C_6H_4\cdot O\cdot CH_3\ (1,\ 4) \\ C_6H_5\cdot CO \end{array}.$$

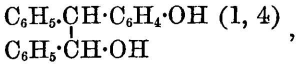
The foregoing method of alkylation was adopted in view of the possibility that the hydrogen-atom of the CH-group might also be replaced by methyl. That no such reaction occurred is in keeping with the observation made by Victor Meyer and Oelkers (*Ber.*, **21**, 1300) that only one hydrogen-atom of the methylene-group in deoxybenzoïn can be replaced by alkyl. In the present case, this first hydrogen-atom is already replaced by the group $—C_6H_4\cdot O\cdot CH_3$; the second does not react.

Reduction with Sodium and Amyl Alcohol.—10 grams of *p*-desylphenol were dissolved in excess of amyl alcohol, and 6·5 grams of metallic sodium were gradually added to the boiling liquid. The amyl alcoholic solution was shaken with dilute hydrochloric acid, washed with water, and distilled down to a small bulk, finally removing the remainder of the amyl alcohol on the water-bath under reduced pressure. The product was recrystallised from benzene, which deposited it in tufts of slender, colourless needles melting constantly at 161—162°. It is soluble in caustic alkalis. Analysis led to the formula $C_{20}H_{18}O_2$:—

	Substance.	CO_2.	H_2O.
I	0·2025	0·6133	0·1124
II	0·2220	0·6725	0·1256

	Calculated for $C_{20}H_{18}O_2$.		Found.	
			I.	II.
C_{20}	240	82·75	82·59	82·61
H_{18}.......	18	6·20	6·16	6·28
O_2	32	11·05	—	—
	290	100·00		

The compound has the constitution



$$\begin{array}{l} C_6H_5\cdot \underset{|}{C}H\cdot C_6H_4\cdot OH\ (1,\ 4) \\ C_6H_5\cdot CH\cdot OH \end{array},$$

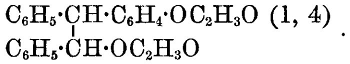
and may be termed *hydrodesylphenol.*

When it is heated with excess of acetic anhydride for three hours at 150°, it yields a diacetyl-derivative. This compound was purified by recrystallisation from a mixture of benzene and light petroleum. It forms groups of needles melting at 156—157°. Analysis gave figures agreeing with the formula $C_{24}H_{22}O_4$:—

	Substance.	CO_2.	H_2O.
I	0·2045	0·5767	0·1080
II.........	0·2008	0·5659	0·1027

	Calculated for $C_{24}H_{22}O_4$.		Found.	
			I.	II.
C_{24}	288	77·00	76·91	76·85
H_{22}.......	22	5·88	5·85	5·68
O_4	64	17·12	—	—
	374	100·00		

It has the constitution

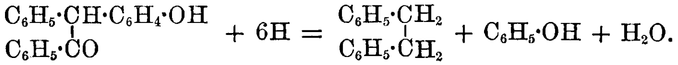


$$\begin{array}{l} C_6H_5\cdot CH\cdot C_6H_4\cdot OC_2H_3O\ (1, 4) \\ C_6H_5\cdot CH\cdot OC_2H_3O \end{array}.$$

Reduction with Hydriodic Acid.—*p*-Desylphenol was heated with fuming hydriodic acid and amorphous phosphorus for four hours at 130°, after which the contents of the tube were poured into water, extracted with ether, and the ethereal solution decolorised with sulphurous acid. The ethereal solution was shaken with caustic soda, to remove any phenolic compound. On acidifying this alkaline solution and distilling with steam, ordinary phenol passed over, which was identified by the precipitate with bromine-water, and the violet coloration with ferric chloride.

On evaporating the ethereal solution, thus freed from phenol, an oil was left, which smelt like dibenzyl, and, after distillation under reduced pressure, solidified. The crystalline mass was dissolved in alcohol, but as nothing separated over night, a minute crystal of dibenzyl was added, when the substance was at once deposited in large laminæ, which, after recrystallisation from alcohol, melted at 52—53° (m. p. of dibenzyl 51·5—52·5°), and gave on analysis figures agreeing with those required for dibenzyl. Calculated for $C_{14}H_{14}$: C 92·30, H 7·69. Found: C 92·10, H 7·80 per cent.

The reduction with hydriodic acid, therefore, takes place according to the equation



$$\begin{array}{l} C_6H_5\cdot CH\cdot C_6H_4\cdot OH \\ C_6H_5\cdot CO \end{array} + 6H = \begin{array}{l} C_6H_5\cdot CH_2 \\ C_6H_5\cdot CH_2 \end{array} + C_6H_5\cdot OH + H_2O.$$

The ease with which this reaction, which, according to this equation, involves a separation of carbon from carbon, occurs at the relatively low temperature of 130° led us at first to doubt whether the desyl-group really was attached to the nucleus of the phenol. The result of the fusion with potash, however, decides this question in the affirmative.

Fusion with Caustic Potash.—*p*-Desylphenol was fused with 10 parts of caustic potash mixed with 1 part of water, and kept at a temperature of 200—210°. At first the fused potassium salt of *p*-desylphenol floated as a yellow liquid on the surface of the potash; but by continually stirring it, it was converted into a pulverulent, grey salt, which was disseminated throughout the mass. At this point the reaction is complete. The melt was dissolved in water, nearly neutralised with hydrochloric acid, and carbon dioxide passed in to precipitate phenols. After separating the precipitate by filtration, hydrochloric acid was added to the filtrate, which was then extracted with ether. On distilling off the ether, a large quantity of benzoic acid was obtained.

The precipitate formed with carbon dioxide was recrystallised from alcohol, and afterwards from a mixture of benzene and petroleum, from which it was deposited in groups of large, flat, obliquely truncated needles melting constantly at 84—85°. Analysis agreed with the formula $C_{13}H_{12}O$.

0·2010 gram gave 0·6252 CO_2 and 0·1178 H_2O.

	Calculated for $C_{13}H_{12}O$.		Found.
C_{13}	156	84·78	84·83
H_{12}	12	6·52	6·51
O	16	8·70	—
	184	100·00	

The compound is identical with *p*-benzylphenol, the melting point of which is given at 84° (Paternò, Rennie). Its formation from *p*-desylphenol may be expressed as follows:—

$$\frac{C_6H_5\cdot CH\cdot C_6H_4\cdot OH}{C_6H_5\cdot CO} \quad \frac{H}{OH} = \frac{C_6H_5\cdot CH_2\cdot C_6H_4\cdot OH}{C_6H_5\cdot COOH}.$$

This reaction proves conclusively that the desyl-group is attached to the nucleus of the phenol, and it may also be taken as showing, so far as the evidence afforded by a potash fusion can be admitted, that desylphenol is a para-derivative.

The decomposition of *p*-desylphenol into benzylphenol and benzoic acid appears also to take place slowly with strong aqueous caustic potash at 100°.

If a higher temperature is employed in the foregoing fusion, the *p*-benzylphenol is in turn broken up, and a mixture of *p*-hydroxybenzoic acid and benzoic acid is obtained. The *p*-hydroxybenzoic acid, after separating it from the benzoic acid, was identified by its melting point, and by the reaction with bromine-water. The yield was good, so that the acid could not have been formed by the oxidation of benzoic acid, as in Barth's experiment on the fusion of benzoic acid with caustic potash (*Annalen*, **164**, 141).

All the foregoing reactions are in harmony with the constitution of the compound as *p*-desylphenol.

We have failed, however, to obtain direct proof of the presence of a ketonic carbonyl-group, as the substance does not react either with phenylhydrazine or with hydroxylamine, although it was treated with these reagents under a variety of the most favourable conditions.

It might be concluded from this that the compound does not contain a carbonyl-group, and exists only in the tertiary or hydroxylic form which it exhibits in its diacetyl-derivative. The high temperature, however, required for the introduction of the second acetyl-group speaks against this view. The inability to react with phenylhydrazine and hydroxylamine is rather, we think, to be explained by the observation of V. Meyer and Oelkers (*Ber.*, **21**, 1299), that the difficulty with which the monalkyl-deoxybenzoïns form hydroximes increases with the molecular weight; thus benzyl-deoxybenzoïn only yielded a hydroxime when heated with hydroxylamine hydrochloride at 150—160°, a treatment by which our compound is totally resinised.

Victor Meyer has shown (*Ber.*, **21**, 1293) that methyldeoxybenzoïn reacts with nitrous acid, eliminating benzoic acid, and yielding acetophenonoxime. Following this analogy, we treated *p*-desylphenol with nitrous acid, hoping to obtain *p*-hydroxybenzophenonoxime and benzoic acid; but no action could be observed.

Oxidation experiments gave inconclusive results. With alkaline permanganate, only benzoic acid was obtained, whilst chromium trioxide in acetic acid solution converted the compound into a reddish-brown, uncrystallisable substance.

We also examined the action of concentrated sulphuric acid on mixtures of benzoïn with various other phenols: thus, with thymol, α-naphthol, resorcinol, and quinol. In every case there appeared to be a reaction, manifested by an intense coloration which neither the benzoïn nor the phenol alone yielded with sulphuric acid; but the products of the reactions were uncrystallisable resins, which were not further examined.

The foregoing investigation was commenced by one of us in conjunction with Mr. F. B. Guthrie, to whom are due the preparation of *p*-desylphenol itself and its monacetyl-derivative, and the establishing of the composition of these compounds. Mr. Guthrie's departure from this country to fill a post in the Colonies prevented him from continuing the work.

Royal College of Science, London.