LIV.—*The Reduction Products of o- and p-Dimethoxybenzoin.*

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THE relationship of compounds of the benzoin type to the parent hydrocarbon is usually ascertained by reduction to the corresponding hydrobenzoin and subsequent treatment of this product with hydrogen iodide. By this process ordinary benzoin is converted into dibenzyl, which must be regarded as the simplest corresponding hydrocarbon.

The case of substituted benzoin offers the possibility of more complex reactions of some interest, and we have made a study of the various reduction products obtained from both *o*- and *p*-dimethoxybenzoin.

o-Dimethoxybenzoin (Trans., 1901, **79**, 668) was converted into the corresponding hydrobenzoin by the action of sodium amalgam, and attempts were made to reduce this compound by means of hydrogen iodide. In this case it seemed probable that the removal of the methoxyl groups from the ortho-position might lead to the union of the two benzene nuclei, with the ultimate formation of dihydrophenanthrene. A similar reduction has recently been carried out by Law (Trans., 1906, **89**, 1517), who obtained 9:10-dihydroxyphenanthrene by the electrolytic reduction of hydrosalicyloin. The reaction in question was, however, unsuccessful, and recourse was finally had to Baeyer's method of reduction, the compound being distilled with zinc dust in a current of hydrogen. Contrary to expectation, the main pro-

duct thus obtained was *p*-dimethyltolane, a result which is at variance with the generally accepted statement that Baeyer's method reduces aromatic oxy-compounds to the parent hydrocarbon. Although it is difficult to speculate accurately as to the progress of reactions which take place at high temperatures, we endeavoured to trace the various stages undergone in this abnormal reduction.

With the object of isolating the intermediate products, the method of reduction was somewhat modified; the zinc dust used was not freed from adherent oxide, and the distillation was conducted at the lowest possible temperature in an atmosphere of carbon dioxide. Under these conditions the methoxyl groups remained unreduced, and the principal product consisted of *o*-dimethoxystilbene:

On further reduction under the same conditions, this substance was converted into a mixture of *o*-dimethoxydibenzyl and *p*-dimethyltolane,

and the latter substance constituted the sole product when the ethane derivative was in turn reduced.

The conversion of the *o*-methoxy-compounds into the *p*-hydrocarbon is therefore effected at the last stage of the reduction, and is in all probability due to the removal of two molecules of water, and subsequent transference of the two methyl groups to the position of greatest stability.

In view of the general importance of Baeyer's method of reduction and the abnormality of the above result, we extended our experiments to anisoin and its derivatives. The compounds selected for experiment were prepared with the object of testing the effect of the reduction on different side chains.

The table on page 538 classifies the results obtained.

The evidence of experiments (1) and (2) shows that the side chains $\begin{smallmatrix} \cdot\text{CH}\cdot\text{OH} \\ \cdot\text{CO} \end{smallmatrix}$ and $\begin{smallmatrix} \cdot\text{CH}\cdot\text{OMe} \\ \cdot\text{CO} \end{smallmatrix}$ reduce alike to $\begin{smallmatrix} \cdot\text{CH}_2 \\ \cdot\text{CO} \end{smallmatrix}$, when the reduction is carried out in carbon dioxide. Moreover, experiments (3) and (4) afford additional proof that the ketonic group, and also the phenolic methoxyl groups remain unaltered under these conditions. On the other hand, reactions (5) and (6) show that the groups $\begin{smallmatrix} \cdot\text{CH}\cdot\text{OH} \\ \cdot\text{CH}\cdot\text{OH} \end{smallmatrix}$ and $\begin{smallmatrix} \text{CH}\cdot\text{OMe} \\ \text{CH}\cdot\text{OH} \end{smallmatrix}$, when similarly treated, reduce first to $\begin{smallmatrix} \cdot\text{CH} \\ \cdot\text{CH} \end{smallmatrix}$. The effect of substituting hydrogen for carbon dioxide in the process is

Substance.	Conditions of experiment.	Products.
1. Anisoin	Distilled in carbon dioxide.	Deoxyanisoin ; trace of <i>p</i> -dimethoxystilbene.
2. Anisoin methyl ether.	„ „ „	Deoxyanisoin ; trace of <i>p</i> -dimethoxystilbene.
3. Deoxyanisoin	„ „ „	Deoxyanisoin.
4. Anisil	„ „ „	Anisil.
5. Hydroanisoin	„ „ „	<i>p</i> -Dimethoxystilbene.
6. Hydroanisoin mono-methyl ether	„ „ „	<i>p</i> -Dimethoxystilbene.
7. Deoxyanisoin	Distilled in hydrogen.	<i>p</i> -Dimethoxystilbene ; stilbene.
8. Hydroanisoin	„ „ „	Stilbene.
9. <i>p</i> -Dimethoxystilbene..	„ „ „	Stilbene.

shown in (7), (8), and (9), and only then is a hydrocarbon obtained. The nature of the complete reduction of anisoin, and its ultimate conversion into stilbene, is best seen if we accept the enolic formula for deoxybenzoin as shown below :

The position occupied by the methoxyl groups in the ring therefore affects the nature of the reduction considerably. Both in the ortho- and para-compounds studied the alkyloxy-groups are evidently the last to be eliminated, but in the former case the methyl groups ultimately effect substitution in the ring, whilst in the latter they are removed, probably in the form of methyl alcohol.

Our results show that the evidence given by Baeyer's reduction process must be accepted with some caution in deducing the constitution of aromatic oxy-compounds. In particular, the irregular reduction undergone by methoxy-derivatives renders the application of this method to the determination of the structural formulæ of many alkaloids extremely doubtful.

EXPERIMENTAL.

Preparation of o-Dimethoxyhydrobenzoin.

The *o*-dimethoxybenzoin required was prepared, as already described (*loc. cit.*), by the condensation of salicylaldehyde methyl ether. The reduction of the compound to a hydrobenzoin was carried out by the action of sodium amalgam on a solution of the benzoin in moist ether. Ninety grams of dimethoxybenzoin were dissolved in ether saturated with

water, and subjected to the action of a large excess of finely powdered 4 per cent. sodium amalgam. A brisk current of carbon dioxide was led into the well cooled solution, which was thoroughly mixed by means of a powerful mechanical stirrer. As the hydrobenzoin is practically insoluble in ether it was precipitated along with the sodium bicarbonate produced in the reaction. After forty-eight hours the liquid was filtered, and the residual sludge, after separation from mercury, was extracted with boiling alcohol. In this way the hydrobenzoin was removed, and, after recrystallisation from alcohol, was obtained in large prisms melting at 153—154°. The ethereal filtrate, on concentration, furnished an additional quantity of the powder, the total yield of which amounted to 70 grams. Analysis gave :

(I) C = 69.82 ; H = 6.60. (II) C = 69.92 ; H = 6.71.

$C_{16}H_{18}O_4$ requires C = 70.07 ; H = 6.57 per cent.

Examination showed that no products corresponding to *isohydrobenzoin* or *deoxybenzoin* were produced in the reaction.

The existence of two hydroxyl groups in the hydrobenzoin was proved by boiling the compound with excess of acetic anhydride. After two hours' treatment, the excess of reagent was removed under diminished pressure, and the residue crystallised from a mixture of alcohol and light petroleum. The product, which crystallised in small prisms, melted at 171—172°, and analysis showed the substance to be the *diacetyl* derivative of the hydrobenzoin.

(I) C = 66.83 ; H = 6.16. (II) C = 67.15 ; H = 6.19.

$C_{20}H_{22}O_6$ requires C = 67.04 ; H = 6.14 per cent.

With a similar object in view, the action of phenylcarbimide on the hydrobenzoin was tried, and we obtained the *diphenylurethane* derivative in beautiful prisms (m. p. 186—187°).

Analysis gave :

C = 70.12 ; H = 5.57 ; N = 5.59.

$C_{30}H_{28}O_6N_2$ requires C = 70.31 ; H = 5.47 ; N = 5.47 per cent.

Reduction of o-Dimethoxyhydrobenzoin.—Several attempts were made in the first place to reduce the compound by means of hydrogen iodide. Experiments carried out at various temperatures ranging from 100° to 200° gave only gummy products, and even at the ordinary temperature the hydrobenzoin was rapidly converted into an uncrystallisable tar when mixed with the concentrated acid. The reduction was therefore carried out by distilling an intimate mixture of the hydrobenzoin and excess of zinc dust over pumice stone with which zinc dust was incorporated. The best yields were obtained when not more than 5 grams of the hydrobenzoin were used in each experiment. The distillation was carried out as usual in a sloping combustion tube, the end of which was fitted with an adapter dipping under alcohol. As

explained in the introduction, the distillation can be controlled so as to give three distinct reduction products. When carried out at the lowest possible temperature in a stream of dry carbon dioxide, the product was an oil which, after repeated fractionation, boiled at 195—197° under 20 mm. pressure, and which did not crystallise when kept at -10° for several days.

Analysis gave :

(I) C=79.90 ; H=6.58. (II) C=80.13 ; H=6.65.

$C_{16}H_{16}O_2$ requires C=80.00 ; H=6.60 per cent.

As the compound behaved as an unsaturated substance towards bromine, and was also not affected by the action of acetic anhydride, it was regarded as *o*-dimethoxystilbene. This view was confirmed by its reduction by the method just described. When distilled over zinc dust it yielded an oil which crystallised on standing. The product was purified from dilute alcohol (prisms, m. p. 83—84°).

Analysis gave :

(I) C=79.26 ; H=7.55. (II) C=79.36 ; H=7.59.

$C_{16}H_{18}O_2$ requires C=79.34 ; H=7.44 per cent.

As acetic anhydride was without action on the compound, it is considered to be *o*-dimethoxydibenzyl.

Both the above substances gave *p*-dimethyltolane when reduced by Baeyer's process, but the most convenient method of preparing the latter compound is to reduce the hydrobenzoin in a current of hydrogen. In this way the intermediate compounds in the reduction are converted into the hydrocarbon. The distillate crystallised readily on cooling, and, after draining from adherent oil on a porous plate, the crystals were purified by recrystallisation from alcohol. The product consisted of long, delicate needles melting at 136—137°, and possessing a beautiful blue fluorescence. The mother liquors from the recrystallisation invariably contained a little *o*-dimethoxydibenzyl, and the oil recovered from the porous plate proved to contain the ethylene derivative.

p-Dimethyltolane.—Considerable trouble was experienced in identifying the compound melting at 136—137° with *p*-dimethyltolane, as the analysis presented great difficulties. Using the ordinary combustion method, the values found for hydrogen were practically constant, but the carbon content showed great variation, ranging from 70 to 85 per cent. The admixture of copper oxide or potassium dichromate with the substance in the boat was without avail, and the substitution of the bayonet tube method was equally unsuccessful. The wet method of combustion (Fritzsche, *Annalen*, 1897, 294, 79) and the Dennstedt process were also tried, but without success. Finally, the substance was burned in the usual way, using a tube

3 metres long. The carbon content still varied somewhat, but the results showed the compound to be a hydrocarbon. The mean value for hydrogen in twelve combustions was 6.99 per cent., and the maximum value found for carbon was 92.96 per cent. ($C_{16}H_{14}$ requires C=93.20; H=6.80 per cent.). The molecular weight, determined by the boiling point method in chloroform solution, was 207 (calculated 206), and the identity of the compound with *p*-dimethyltolane was further established by the preparation of the latter from *p*-dimethylstilbene dibromide. The specimen thus obtained melted, as did the compound under examination, at 136° , and a mixture of the two preparations melted sharply at the same temperature.

In view of the difficulties described above, it is a significant fact that in the original preparation of this compound (*Ber.*, 1873, 6, 1505) no analyses are quoted.

o-Dimethoxybenzil.—It was considered advisable to substantiate the ortho-character of the various compounds in view of their ultimate reduction to a para-hydrocarbon. In the case of *o*-dimethoxybenzoin this has already been done (*loc. cit.*) in its conversion into *o*-methoxybenzoic acid, and similar evidence was therefore sought in the case of dimethoxyhydrobenzoin.

When boiled with alkaline potassium permanganate solution the compound underwent ready oxidation. After twelve hours' treatment the liquid was filtered, and the residue, after drying, was extracted with boiling ether. The extract on evaporation deposited a crop of well-formed, colourless prisms melting at 127° , which analysis showed to be dimethoxybenzil:

(I) C=70.96; H=5.31. (II) C=71.18; H=5.38.

$C_{16}H_{14}O_4$ requires C=71.11; H=5.18 per cent.

As dimethoxybenzoin gives the same product in almost quantitative amount under these conditions, the ortho nature of the hydrobenzoin is in this way confirmed. This method of preparing the benzil by the action of potassium permanganate is more advantageous than the commoner process of treatment with nitric acid, as in the latter case the by-products are not only troublesome to remove by crystallisation, but are highly explosive.

That the dimethoxybenzil was the ortho-compound was in turn confirmed by its reaction with fused potassium hydroxide. No compound corresponding to benzilic acid was formed, and the product, after acidification with hydrochloric acid, was found to contain only salicylic acid.

Reduction of Anisoin by Baeyer's Method.

This reaction was carried out exactly as already described for *o*-dimethoxyhydrobenzoin, a current of carbon dioxide being employed

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in the first instance. The product was an oil which crystallised completely on cooling. On recrystallisation from hot alcohol a small first crop was obtained consisting of leaflets which melted at $205-207^{\circ}$, but the bulk of the product, amounting to 80 per cent. of the substance used, separated in long needles. The latter compound was treated with cold ethyl acetate, and in this way freed from traces of the product of higher melting point which remained undissolved. After removal of the solvent the residue was crystallised from hot alcohol, the compound then melting at $108-109^{\circ}$.

Analysis showed the substance to be deoxyanisoin :

C = 75.07 ; H = 6.38 ; OMe = 26.0.

$C_{16}H_{16}O_3$ requires C = 75.00 ; H = 6.25 ; OMe = 25.6 per cent.

As Russell (*Annalen*, 1869, 151, 25) quotes 95° as the melting point of deoxyanisoin, and as, moreover, isohydroanisoin melts at 110° , the substance was further examined. The molecular weight was determined in benzene by the cryoscopic method, and gave the value 240 (calculated 256). The compound, moreover, had no action on Fehling's solution, and was recovered unchanged when boiled with either acetic anhydride or dilute sulphuric acid. When boiled with alkaline potassium permanganate it was converted into anisil (m. p. 133°). The presence of the ketonic group was shown by the action of hydroxylamine. The compound was boiled for three hours in methyl-alcoholic solution with the calculated amount of the base. The solution was poured into water, and the crystalline precipitate separated, dried, and recrystallised from a mixture of benzene and light petroleum.

Analysis of the product, which crystallised in needles melting at $120-121^{\circ}$, showed it to be the oxime of deoxyanisoin :

C = 70.68 ; H = 6.48.

$C_{16}H_{17}O_3N$ requires C = 70.85 ; H = 6.27 per cent.

As already mentioned, the reduction of anisoin also yielded a small quantity of a compound melting at $205-207^{\circ}$.

Analysis gave :

C = 79.95 ; H = 6.87 ; OMe = 26.80.

$C_{13}H_{16}O_2$ requires C = 80.00 ; H = 6.60 ; OMe = 25.83 per cent.

As, in addition, the compound gave a bromine derivative melting at $118-120^{\circ}$, it is evidently *p*-dimethoxystilbene.

Both deoxyanisoin and dimethoxystilbene were found to distil unchanged when heated with zinc dust in a stream of carbon dioxide, but in an atmosphere of hydrogen each compound was converted into stilbene. The latter was identified by its melting point (124°) and its conversion into α -stilbene dibromide (m. p. 237°).

Preparation and Reduction of Anisoin Derivatives.

Anisoin Methyl Ether.—This compound was prepared by the silver oxide method in the manner already described for the corresponding ortho-compound (*loc. cit.*). The addition of a little dry acetone was necessary to effect complete solution of the anisoin in the methyl iodide. The product crystallised readily in pale yellow prisms, which after recrystallisation from carbon tetrachloride melted at 52–53°. The yield was quantitative. The compound is very soluble in ether, acetone, or benzene; a cold saturated alcoholic solution, on heating to about 60°, deposits a portion of the dissolved compound as an oil, which, however, redissolves at higher temperatures.

Analysis gave :

C = 71.38 ; H = 6.26 ; OMe = 31.8.

C₁₇H₁₈O₄ requires C = 71.32 ; H = 6.29 ; OMe = 32.5 per cent.

As the compound is much more volatile than anisoin, the reduction with zinc dust had to be conducted more slowly. As already explained, the same reduction products were obtained as in the case of anisoin.

Hydroanisoin Monomethyl Ether.—The reduction of the ketonic group in anisoin methyl ether was effected by the action of sodium amalgam with the production of the corresponding hydrobenzoin methyl ether. The details of the process were the same as already described for the preparation of *o*-dimethoxyhydrobenzoin. The product crystallised in complicated prisms (m. p. 98–99°) from a concentrated solution in ethyl alcohol.

Analysis gave :

C = 70.57 ; H = 7.03 ; OMe = 31.63.

C₁₇H₂₀O₄ requires C = 70.83 ; H = 6.94 ; OMe = 32.29 per cent.

In this case also the reduction by Baeyer's process was carried out slowly on account of the volatility of the compound. The reduction yielded *p*-dimethoxystilbene.

Hydroanisoin.—This compound is best prepared by the action of sodium amalgam on an ethereal solution of anisoin, the separation of the product from the sodium bicarbonate being effected by extraction with absolute alcohol. The yield of pure product (m. p. 167–169°) was more than 71 per cent. of the theoretical amount, and no *iso*-hydroanisoin or deoxyanisoin was produced. Reduction with zinc dust gave *p*-dimethoxystilbene as the sole product when the reaction was carried out in an atmosphere of carbon dioxide. When a current of hydrogen was used the reduction proceeded further and stilbene was the main product.

Deoxyanisoin.—We found it more convenient to prepare the necessary deoxyanisoin by the distillation of a mixture of zinc dust and

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anisoin in a current of carbon dioxide. The product was separated as already described from traces of *p*-dimethoxystilbene by solution in cold ethyl acetate. This method of preparation gives a better yield and purer product than that obtained by the decomposition of hydro-anisoin by means of sulphuric acid.

Anisil.—The anisil required was prepared from anisoin by boiling for two hours with a solution of the calculated amount of alkaline potassium permanganate. The residue obtained on filtration was extracted with boiling ether. In this way the diketone was obtained in almost quantitative amount in pale yellow needles melting at 133°. The method possesses obvious advantages over the alternative process, in which nitric acid is used as the oxidising agent.

We are extending our work on the mechanism of Baeyer's reduction process, and have obtained further results, which we hope to publish shortly.

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