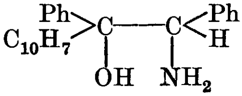
CCVIII.—*The Dehydration of Glycols derived from α-Naphthylglycollic Acid.*

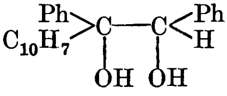
By Alex. McKenzie and Walter Samuel Dennler.

The present investigation arose from previous work on the deamination of 2-hydroxy-1 : 2-diphenyl-2-α-naphthylethylamine (I) and on the dehydration of α-naphthylhydrobenzoin (II) (McKenzie and Richardson, J., 1923, **123**, 79; McKenzie and Roger, J., 1924, **125**, 844; McKenzie and Dennler, *ibid.*, p. 2105; Tiffeneau and Orékhov, *Compt. rend.*, 1924, **178**, 1619). It appeared likely that 1-*α-naphthyl*-2 : 2-*diphenylethylene glycol* (III), which is isomeric with (II), would behave very differently when acted on by sulphuric acid. By arrangement with Professor Tiffeneau, it is now shown in the present paper that this is the case.



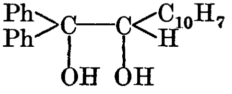
$$\genfrac{}{}{0pt}{}{Ph}{C_{10}H_7}\!>\!\underset{OH}{\underset{|}{C}}\!-\!\!-\!\underset{NH_2}{\underset{|}{C}}\!<\!\genfrac{}{}{0pt}{}{Ph}{H}$$

(I.)



$$\genfrac{}{}{0pt}{}{Ph}{C_{10}H_7}\!>\!\underset{OH}{\underset{|}{C}}\!-\!\!-\!\underset{OH}{\underset{|}{C}}\!<\!\genfrac{}{}{0pt}{}{Ph}{H}$$

(II.)



$$\genfrac{}{}{0pt}{}{Ph}{Ph}\!>\!\underset{OH}{\underset{|}{C}}\!-\!\!-\!\underset{OH}{\underset{|}{C}}\!<\!\genfrac{}{}{0pt}{}{C_{10}H_7}{H}$$

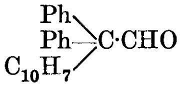
(III.)

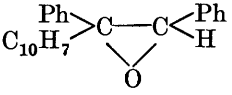
The products resulting from the elimination of water from (II) have already been shown to depend on the experimental conditions. With cold concentrated sulphuric acid, both α-naphthyldeoxybenzoin (IV) and diphenylacetonaphthone (V) were formed, whereas with hot dilute sulphuric acid the products were α-naphthyldeoxybenzoin

(IV), diphenyl-α-naphthylacetaldehyde (VI), and diphenyl-α-naphthylethylene oxide (VII).

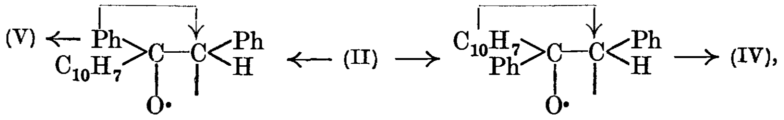
$C_{10}H_7{\cdot}CHPh{\cdot}COPh$
(IV.)

$C_{10}H_7{\cdot}CO{\cdot}CHPh_2$
(V.)

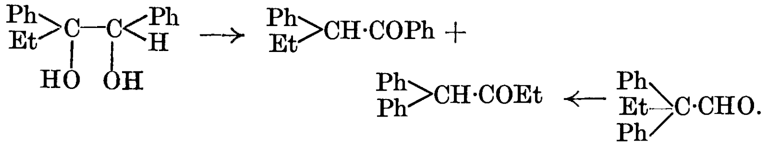

(VI.)


(VII.)

Whilst the formation of both (IV) and (V) from (II) may be interpreted on the basis of semipinacolinic transposition,

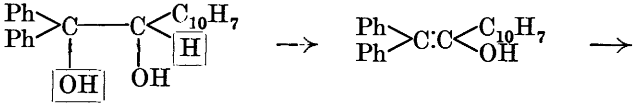


it should be noted that Danilov (*J. Russ. Phys. Chem. Soc.*, 1919, **51**, 97) has shown that triphenylacetaldehyde undergoes molecular rearrangement into phenyldeoxybenzoin even under the influence of hot dilute sulphuric acid, thus : $CPh_3{\cdot}CHO \longrightarrow CHPh_2{\cdot}COPh$. Similarly, Orékhov and Tiffeneau (*Compt. rend.*, 1926, **182**, 67) have shown that substituted acetaldehydes undergo transformation into the same ketones as are formed by the direct dehydration of the corresponding glycols, *e.g.*, a mixture of ethyldeoxybenzoin and diphenylbutanone is obtained either from diphenylethylacetaldehyde or from ethylhydrobenzoin :



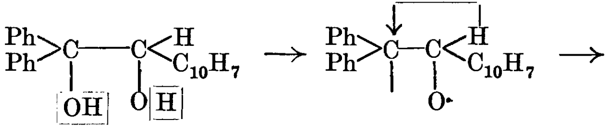
In the light of these results, it would appear quite probable that, in the formation of (IV) and (V) from (II), the intermediate product might be (VI). The proportion of (IV) and (V) in the mixture resulting from the dehydration of (II) with cold concentrated sulphuric acid varies according to the experimental conditions, and it might not be easy to arrive at this proportion experimentally, more particularly since the ketones melt at practically the same temperature. The recent work of Luce (*Compt. rend.*, 1925, **180**, 145), however, would indicate that the migrational aptitude of α-naphthyl is greater than that of phenyl, and one would argue that, in the mixture of ketones referred to, (IV) should preponderate.

1-α-Naphthyl-2 : 2-diphenylethylene glycol was prepared by the action of magnesium phenyl bromide on methyl α-naphthylglycollate. It gave the same ketone, namely, diphenylacetonaphthone (V), irrespective as to whether cold concentrated sulphuric acid or hot dilute sulphuric acid was used as the dehydrating agent, and its behaviour is thus quite different from that of the isomeric glycol (II). The change, which is best depicted as a vinyl dehydration, involves no transposition of phenyl:



$$\mathrm{Ph_2C(\boxed{OH})\!-\!C(OH)(C_{10}H_7)\boxed{H}} \longrightarrow \mathrm{Ph_2C{:}C(C_{10}H_7)OH} \longrightarrow \text{(V.)}$$

Since phenyl has undoubtedly a stronger saturation capacity than α-naphthyl, the sum of the saturation capacities of the two phenyls will be greater than that of α-naphthyl plus hydrogen. The alternative explanation,

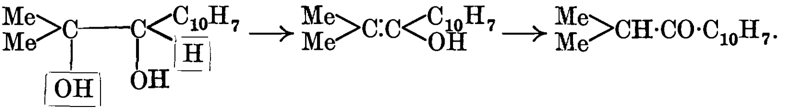


$$\mathrm{Ph_2C(\boxed{OH})\!-\!C(H)(C_{10}H_7)O\boxed{H}} \longrightarrow \mathrm{Ph_2C\!-\!C(H)(C_{10}H_7)O{\cdot}} \longrightarrow \text{(V.)}$$

which involves migration of hydrogen in preference to α-naphthyl, is regarded as unsatisfactory.

The researches of both Meerwein and Tiffeneau have demonstrated that phenyl has a strong saturation capacity, and a comparison of the results obtained by dehydrating (II) and (III) will show that the saturation capacity of phenyl is greater than that of α-naphthyl. Obviously, the dehydration of (III) is not a semipinacolinic change; if it were, the product would be (IV) and not (V). Of the two hydroxyls, the tertiary is the more loosely bound, because the saturation capacity of the two phenyl groups more than balances the saturation capacity of α-naphthyl plus hydrogen.

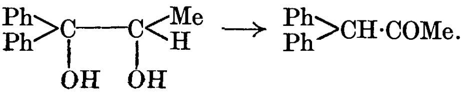
1-α-*Naphthyl*-2 : 2-*dimethylethylene glycol* was prepared from methyl α-naphthylglycollate and magnesium methyl iodide. Its behaviour on dehydration is similar to that of (III):



$$\mathrm{Me_2C(\boxed{OH})\!-\!C(OH)(C_{10}H_7)\boxed{H}} \longrightarrow \mathrm{Me_2C{:}C(C_{10}H_7)OH} \longrightarrow \mathrm{Me_2CH{\cdot}CO{\cdot}C_{10}H_7}.$$

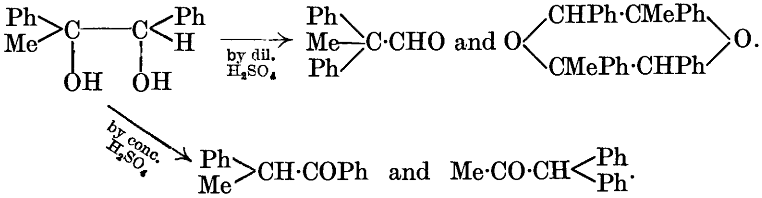
This result was anticipated, since methyl has a strong saturation capacity.

The behaviour of (III) and (II) on dehydration has a parallel in two other cases which may be quoted. Thus, diphenylpropylene glycol gives diphenylacetone both with hot dilute and with cold concentrated sulphuric acid:



$$\mathrm{Ph_2C(OH)\!-\!C(OH)(Me)H} \longrightarrow \mathrm{Ph_2CH{\cdot}COMe}.$$

The isomeric methylhydrobenzoin, however, behaves differently :

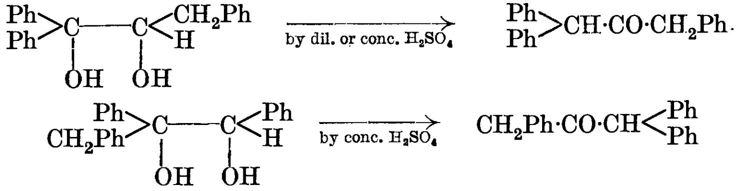


$$\mathrm{{Ph \atop Me}{>}\underset{OH}{C}{-\!\!-}\underset{OH}{C}{<}{Ph \atop H}} \xrightarrow[\text{by dil. } H_2SO_4]{} \mathrm{{Ph \atop {Me \atop Ph}}{>}C{\cdot}CHO} \text{ and } \mathrm{O{<}{CHPh{\cdot}CMePh \atop CMePh{\cdot}CHPh}{>}O.}$$

$$\xrightarrow[\text{by conc. } H_2SO_4]{} \mathrm{{Ph \atop Me}{>}CH{\cdot}COPh} \text{ and } \mathrm{Me{\cdot}CO{\cdot}CH{<}{Ph \atop Ph}}.$$

(For literature, see McKenzie and Roger, *loc. cit.*)

Again, *as*-benzyldiphenylethylene glycol may be contrasted with the isomeric benzylhydrobenzoin :



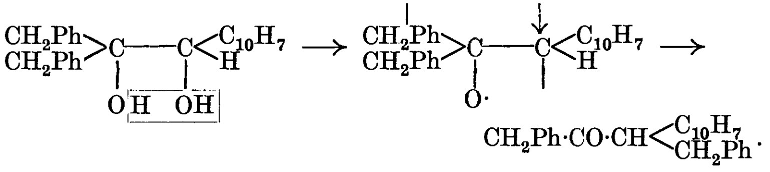
$$\mathrm{{Ph \atop Ph}{>}\underset{OH}{C}{-\!\!-}\underset{OH}{C}{<}{CH_2Ph \atop H}} \xrightarrow[\text{by dil. or conc. } H_2SO_4]{} \mathrm{{Ph \atop Ph}{>}CH{\cdot}CO{\cdot}CH_2Ph}.$$

$$\mathrm{{Ph \atop CH_2Ph}{>}\underset{OH}{C}{-\!\!-}\underset{OH}{C}{<}{Ph \atop H}} \xrightarrow[\text{by conc. } H_2SO_4]{} \mathrm{CH_2Ph{\cdot}CO{\cdot}CH{<}{Ph \atop Ph}}$$

(Orékhov, *Bull. Soc. chim.*, 1919, **25**, 107).

Here the same ketone is produced by two different mechanisms, migration of phenyl taking place in the one case and not in the other.

The ketones formed from 1-α-naphthyl-2 : 2-diphenylethylene glycol and 1-α-naphthyl-2 : 2-dimethylethylene glycol, respectively, cannot exist in optically active modifications. To obtain such a ketone from a glycol derived from optically active α-naphthylglycollic acid, it would be necessary for semipinacolinic change to occur during the dehydration of the glycol instead of the vinyl dehydration as in the two other cases, and even then optical activity might not persist. Accordingly, since Tiffeneau and Lévy (*Bull. Soc. chim.*, 1923, **33**, 759) have shown that benzyl has a greater migrational aptitude than methyl and also has a weaker saturation capacity, the examination of the dehydration of 1-α-*naphthyl*-2 : 2-*dibenzylethylene glycol* (VIII), prepared by the action of magnesium benzyl chloride on methyl α-naphthylglycollate, was undertaken. The change is apparently semipinacolinic :



$$\mathrm{{CH_2Ph \atop CH_2Ph}{>}\underset{OH}{C}{-\!\!-}\underset{OH}{C}{<}{C_{10}H_7 \atop H}} \longrightarrow \mathrm{{CH_2Ph \atop CH_2Ph}{>}\underset{O\cdot}{C}{-\!\!-}C{<}{C_{10}H_7 \atop H}} \longrightarrow \mathrm{CH_2Ph{\cdot}CO{\cdot}CH{<}{C_{10}H_7 \atop CH_2Ph}}.$$

EXPERIMENTAL.

Preparation of α-Naphthylglycollic Acid.—(1) *From α-naphthoic acid.* Boessneck's method (*Ber.*, 1883, **16**, 639) was modified as follows: α-Naphthoic acid (40 g.) ⟶ acid chloride (37 g.), b. p. 170—172°/15 mm., ⟶ α-naphthoyl cyanide (27 g.), m. p. 100°, ⟶ α-naphthoylformamide (24 g.), m. p. 151—153°, ⟶ α-naphthoylformic acid (15 g.), m. p. 110—111°. The latter acid was reduced by aluminium turnings and an excess of caustic potash, the excess of aluminium removed, and the hydroxy-acid obtained by acidification by hydrochloric acid and extraction with ether. It crystallised from benzene in rectangular needles, m. p. 80—82°, and was then dried in a vacuum. Yield: 14 g.; m. p. 98·5—99·5° (Found: C, 71·2; H, 5·0. Calc.: C, 71·3; H, 5·0%). Boessneck does not quote the melting point of his acid, but Brandis (*Ber.*, 1889, **22**, 2148), who obtained the acid from α-naphthaldehyde by the cyanohydrin method, gives m. p. 80—81°.

(2) *From naphthalene.* α-Naphthyl methyl ketone (14 g.), prepared from naphthalene by the Friedel and Crafts reaction (Caille, *Compt. rend.*, 1911, **153**, 393), was brominated (Schweitzer, *Ber.*, 1891, **24**, 549). Caustic potash (25 g. in 250 c.c. of water) was added to the dibromide and, after a fortnight, the acid obtained by acidification and extraction with ether was crystallised from benzene (yield of dry acid, 5 g.; m. p. 98—99°. Schweitzer gives m. p. 91—93°).

(3) *From chloral* (compare Hébert, *Bull. Soc. chim.*, 1920, **27**, 45). The Grignard reagent prepared from 150 g. of α-bromonaphthalene (1 mol.) was cooled to −12°, and an ethereal solution of 98 g. of anhydrous chloral (1 mol.) gradually added (90 min.). The action was very vigorous, the ether assumed a blood-red tint, and a solid separated. The mixture remained at 0° over-night, and was then decomposed by ice and dilute acetic acid. The oil resulting from the ethereal solution was mixed with an excess of sodium carbonate, and, after hydrolysis of the trichloro-alcohol and removal of the naphthalene by steam, the aqueous solution was acidified by concentrated hydrochloric acid, and the hydroxy-acid extracted with ether (yield: 70 g.). The acid after crystallisation from benzene and drying in a vacuum melted at 98—99°. Its *silver* salt gave Ag, 35·0 (Calc.: Ag, 35·0%).

Of those three methods, the third was in our experience the most practicable.

α-Naphthylglycollic acid gives a blue coloration when a trace is added to cold concentrated sulphuric acid. Its methyl ester is sparingly soluble in light petroleum, from which it separates in needles, m. p. 79°, as given by Schweitzer (*loc. cit.*) (Found: C, 72·2; H, 5·6. Calc.: C, 72·2; H, 5·6%). When heated under pressure at 100° with aqueous ammonia (*d* 0·88), the ester was converted into *α-naphthylglycollamide*, $C_{10}H_7{\cdot}CH(OH){\cdot}CO{\cdot}NH_2$, which crystallises from acetone–light petroleum in rhombic plates, m. p. 134—135° (Found : C, 71·8; H, 5·7. $C_{12}H_{11}O_2N$ requires C, 71·7; H, 5·5%). An attempt to prepare the ketol, $C_{10}H_7{\cdot}CH(OH){\cdot}CO{\cdot}C_6H_5$, by the action of an excess of magnesium phenyl bromide on the acid amide led to the regeneration of the latter.

Action of Grignard Reagents on Methyl α-Naphthylglycollate.

Action of Magnesium Phenyl Bromide.—An ethereal solution of 5 g. of the ester (1 mol.) was added during 45 minutes to the Grignard reagent prepared from 16 g. of bromobenzene ($4\frac{1}{2}$ mols.). A solid separated during the heating (9 hours). The product was decomposed with ice and ammonium chloride and, after the usual manipulation, diphenyl was removed by light petroleum. The 1-α-*naphthyl*-2 : 2-*diphenylethylene glycol* (III) obtained crystallised from light petroleum (b. p. 60—100°), in which it was sparingly soluble, in rectangular needles, m. p. 126—127° (yield 6·1 g.). It gives a bright green coloration with concentrated sulphuric acid. For analysis, it was dried in a vacuum at 80° (Found : C, 84·6; H, 6·0. $C_{24}H_{20}O_2$ requires C, 84·7; H, 5·9%).

Action of Magnesium Methyl Iodide.—The conditions were similar to the preceding (15 g. of the ester [1 mol.]; Grignard reagent prepared from 60 g. of methyl iodide [6 mols.]; decomposition with ice, ammonium chloride and ammonia). The crude product was crystallised twice from light petroleum, 1-α-*naphthyl*-2 : 2-*dimethylethylene glycol*, $C_{10}H_7{\cdot}CH(OH){\cdot}CMe_2{\cdot}OH$, being obtained (11 g.) in clumps of rectangular prisms, m. p. 81·5—82° (Found : C, 78·0; H, 7·5. $C_{14}H_{16}O_2$ requires C, 77·8; H, 7·5%). It gives a reddish-brown coloration with concentrated sulphuric acid.

Action of Magnesium Benzyl Chloride.—An ethereal solution of 14 g. of the ester (1 mol.) was added during 90 minutes to the Grignard reagent prepared from 40 g. of benzyl chloride ($4\frac{1}{2}$ mols.). A solid separated during the heating (10 hours). The product was decomposed with ice and dilute sulphuric acid, and dibenzyl removed by light petroleum. The 1-α-*naphthyl*-2 : 2-*dibenzylethylene glycol* (VIII) obtained crystallised from rectified spirit in rectangular plates (17 g.), m. p. 174—175° (Found : C, 84·8; H, 6·7. $C_{26}H_{24}O_2$ requires C, 84·8; H, 6·6%). It gives a purple coloration with concentrated sulphuric acid.

Dehydration of Glycols derived from Methyl α-Naphthylglycollate.

Dehydration of the Diphenyl Glycol.—(a) *With concentrated sulphuric acid.* 2 G. of finely-powdered 1-α-naphthyl-2 : 2-diphenylethylene glycol were triturated in instalments with 30 c.c. of concentrated sulphuric acid during 2 hours. The bright green coloration which appeared at first changed gradually to a greenish-brown. The mixture was added to 100 g. of ice, and the ethereal extract dried with sodium sulphate. The resulting oil gradually solidified, and the solid crystallised from rectified spirit in glistening rhombic plates, m. p. 108—109°. The compound (0·9 g.) was identified as diphenylacetonaphthone by its colour reaction with concentrated sulphuric acid, and by the non-depression of melting point when mixed with a specimen of the ketone prepared by the dehydration of α-naphthylhydrobenzoin with concentrated sulphuric acid (McKenzie and Roger, *loc. cit.*).

(b) *With dilute sulphuric acid.* A mixture of the glycol (2 g.), water (16 c.c.), and concentrated sulphuric acid (20 g.) was boiled for 2 hours under reflux. The mixture was cooled, diluted with water, and the oil extracted with ether. The product was crystallised from ethyl alcohol, and diphenylacetonaphthone (1·5 g.), identified as above, was isolated.

Dehydration of the Dimethyl Glycol.—(a) *With concentrated sulphuric acid.* 7 G. of 1-α-naphthyl-2 : 2-dimethylethylene glycol were dehydrated with 100 c.c. of concentrated sulphuric acid. 2 G. of a golden-yellow oil, b. p. 295—298°, were collected.

(b) *With dilute sulphuric acid.* 10 G. of the glycol were boiled for 2½ hours with a mixture of 100 g. of concentrated sulphuric acid and 100 c.c. of water. The resulting oil was fractionated, and the portion boiling at 304—306°/758 mm. was collected. It did not reduce Fehling's solution, nor did it restore the colour to Schiff's reagent. Yield 6 g. (Found : C, 85·3 ; H, 7·0. Calc. for $C_{14}H_{14}O$: C, 84·8 ; H, 7·1%). This was *iso*propyl α-naphthyl ketone, which according to Rousset (*Bull. Soc. chim.*, 1896, **15**, 66) has b. p. 308—310°. The scission of the oil with alcoholic potash gave a solution of potassium salt from which α-naphthoic acid was isolated, and the oil from the dehydration with concentrated sulphuric acid underwent a similar decomposition.

Dehydration of the Dibenzyl Glycol.—(a) *With concentrated sulphuric acid.* 10 G. of 1-α-naphthyl-2 : 2-dibenzylethylene glycol were gradually added (1 hour) with constant trituration to 220 g. of concentrated sulphuric acid. A purple coloration was noted. After being kept for 2 hours at the ordinary temperature, the mixture was poured into 500 g. of ice; the purple coloration then disappeared and the temperature fell quickly to −2°. When the ice had melted, the oil was extracted with ether, the ether expelled, and the residue (7 g.) distilled under diminished pressure. The *compound*, $C_{26}H_{22}O$, was a golden-yellow oil, b. p. 275°/15 mm. For analysis, it was dried in a vacuum (Found : C, 89·3 ; H, 6·3. $C_{26}H_{22}O$ requires C, 89·2 ; H, 6·2%). It solidified after several days, and was then crystallised from rectified spirit, from which it separated in rhombic plates, m. p. 58—59°. With concentrated sulphuric acid, it gave a light brown coloration which disappeared quickly.

(b) *With dilute sulphuric acid.* A mixture of the glycol (15 g.), water (125 c.c.), and concentrated sulphuric acid (120 g.) was boiled for about 2½ hours under reflux, and the oil extracted with ether. The product was an oil (13·5 g.), b. p. 276°/15 mm., which gradually solidified; m. p. 58—59°.

The substance is probably benzyl-α-naphthylmethyl benzyl ketone, $CH_2Ph{\cdot}CO{\cdot}CH(C_{10}H_7){\cdot}CH_2Ph$, but the evidence for its constitution is not quite convincing. It formed no oxime with hydroxylamine, and it is very stable towards alcoholic soda; thus, when 2·5 g. were heated at 100—140° for 24 hours with a solution of 6 g. of caustic soda in ethyl alcohol, the original substance was recovered. It gave, however, benzoic acid when it was oxidised in glacial acetic acid solution with chromic anhydride. The first product of the oxidation was presumably phenylacetic acid; it was found that the latter does give benzoic acid when oxidised under similar conditions to those adopted for the compound.

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