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**Abstract**

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## On the Dehydration of Symmetrical Naphthyl-Substituted Hydroxyglutaric Acids

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In one of our previous works ([1]) it was shown that the dehydration of 1,2,3-triphenyl-2-hydroxyglutaric acid with concentrated sulfuric acid is a convenient route for obtaining 4-phenyl-3-hydroxy-1,2-benzfluorenone. To obtain analogs of the latter with a larger number of fused rings, it was necessary to dehydrate naphthyl-substituted hydroxyglutaric acids. We attempted to obtain the latter from phenyl- and 1- and 2-naphthylacetic acids and from benzoyl chloride and 1- and 2-naphthol by the method of Ivanov and Nikolov ([2]). It turned out, however, that naphthyl-substituted hydroxyglutaric acids are obtained only in the case when the starting products do not contain a 1-naphthyl radical ([3]). As a result, we succeeded in obtaining only the following three hydroxyglutaric acids: 1,3-diphenyl-2-(2′-naphthyl)-, 1,3-(2′,2″-dinaphthyl)-2-phenyl-, and 1,2,3-(2′,2″,2‴-trinaphthyl)-2-hydroxyglutaric acids. The aim of the present work is to study the dehydration of these three acids.

Experiments on the dehydration of 1,3-diphenyl-(2′-naphthyl)-2-hydroxyglutaric acid, carried out by the method described in ([1]) (under the action of 97% $H_2SO_4$ for 20 min), led chiefly to the formation of non-salting-out polysulfo acids and, in small amount, monosulfo acids. We therefore shortened the time of action of sulfuric acid on the hydroxy acid to 2 min. For separation of the compounds formed (neutral products, hydroxyfluorenones, carboxylic acids, monosulfo acids, and polysulfo acids), we used the general method described below (see experiment 1).

In experiments with diphenylnaphthyl-hydroxyglutaric acid we succeeded, by the usual method, in isolating from the bicarbonate solution about 12% of carboxylic acids. From the alkaline and corresponding aqueous solution a resin is isolated, from which, after column chromatography, one of the isomers of 4-phenyl-3-hydroxydibenzfluorenone was obtained, with m.p. 214–214.5°, which we named hydroxydibenzfluorenone A (yield 7.7%). On dissolution in concentrated $H_2SO_4$, A gives a reddish-brown coloration, and in aqueous alcoholic NaOH, a blue-violet one. On acidification of this alkaline solution, a precipitate of unchanged hydroxydibenzfluorenone separates. The neutral ethereal solution gave a mixture of crystals with oil. From it, after column chromatography, a product with m.p. 51–52° was obtained, probably corresponding to the

hydrocarbon (1,3-diphenyl-2-(2′-naphthyl)-propene-1) (yield 2.7%) and benzyl 2-naphthyl ketone, possibly formed after decomposition of the initial hydroxyglutaric acid to naphthoylphenylacetic acid and decarboxylation of the latter.

In order to increase the yield of hydroxydibenzfluorenones, we subjected the obtained monosulfo acid to desulfonation by the method described by one of us ([4]). After treating the resulting mixture by the usual method, we isolated, along with a small amount of carboxylic acids, another isomer, 4-phenyl-3-hydroxydibenzfluorenone—golden-yellow acicular crystals with m.p. 273.5–274°, which we designated as hydroxydibenzfluorenone B (yield 13.5%). In concentrated $H_2SO_4$, B gives a violet coloration, and on dissolution in aqueous alcoholic NaOH, a raspberry-red one. From the neutral solutions, by column chromatography, we separated one of the isomers of 2-phenyl-3-benzylbenzindone, which we named 2-phenyl-3-benzylbenzindone C—orange crystals with m.p. 162.5–163° (yield 23.5%). In concentrated $H_2SO_4$ this product gives a dark-green coloration, is insoluble in aqueous alcoholic NaOH, and is unchanged on treatment in a sealed tube with $CH_3COOH$ saturated with HBr ([5]). The formation of these

products can be explained by the following scheme:

dehydration and decarboxylation scheme for the 2-naphthyl-substituted hydroxyglutaric acid, showing formation of products $(I)$, $(II)$, $(III)$, $(IV)$, $(V)$, $(VI)$, $(VII)$, with elimination of $H_2O$ and $CO_2$.

It follows from this scheme that 4-phenyl-3-hydroxybenzfluorenone A and B each have one condensed benzene nucleus in the 1,2 position and differ in the position of the second condensed benzene nucleus, for which the 5,6 position is excluded because of the presence of the 2-naphthyl radical in the starting acid. On the basis of the same considerations, the formation of 2-phenyl-3-benzylbenzindanone C with the condensed benzene nucleus in the 4,5 position must be excluded. Since the yield of hydroxybenzfluorenone B is almost twice as large as that of A, we may regard it as probable that B should be assigned structure II (i.e., formation as a result of $\alpha$-cyclization). Then structure I remains as the probable structure for A. Since $\alpha$-cyclization is the more probable, it may be assumed that benzindanone C has structure III. It should be emphasized that these considerations concerning the structure of the products obtained are of a very general character and do not yet give sufficient grounds for assigning the corresponding structures to them. Elucidation of their structure will be the task of further investigations. In order to increase the yield of hydroxybenzfluorenone, experiments were carried out with polyphosphoric acid ([6]) (heating for 1 hour at 100° and for 2 hours at 120°) and phosphorus oxychloride ([7]) as dehydrating agents. The results obtained after treatment as in experiment 1 show that these water-removing agents are still less suitable in both cases: along with a large amount of carbonic acids, the main product is a light-yellow resin consisting of

the corresponding hydrocarbon and ketone, while hydroxybenzfluorenones are formed in insignificant amounts.

In the dehydration of 1,3-(2′, 2″-dinaphthyl)-2-phenyl-2-hydroxyglutaric acid by the described method with concentrated sulfuric acid, we obtained products whose yields are also given in Table 1.

Since we were unable to isolate crystals from the resin obtained after acidification of the alkaline and corresponding aqueous extracts, we judged its composition by the raspberry-red coloration which it gives in aqueous-alcoholic NaOH and by its IR spectrum.* In the latter, the two bands at 1692 and 1700 $cm^{-1}$ are, in all probability, due to two isomeric fluorenones. The band at 3520 $cm^{-1}$ indicates a tertiary hydroxyl group in them. For the same reasons, only an IR spectrum was recorded for the neutral resin. In it we found a band similar to that given by 2-phenyl-3-benzylindanone, and a band characteristic of a double bond. On desul-

* All IR spectra were obtained in the laboratory of spectral analysis of the Institute of Organic Chemistry of the Bulgarian Academy of Sciences. Iv. Yuzhnovskii helped us in their interpretation, for which we express our gratitude to him.

Table 1

| | Yield of products upon dehydration of crude 1,3-diphenyl-(2′-naphthyl)-2-oxyglutaric acid, containing 53.1% pure acid, with a water-removing agent (%) | Yield of products upon dehydration of crude 1,3-(2′,2″-dinaphthyl)-2-phenyl-2-oxyglutaric acid, containing 40.3% pure acid, with a water-removing agent (in %) | Yield of products upon dehydration of crude 1,2,3-(2′,2″,2‴-trinaphthyl)-2-oxyglutaric acid, containing 15.4% pure acid, with a water-removing agent (in %) |
|---|---|---|---|
| | $POCl_3$ | polyphosphoric acid | $H_2SO_4$ |
| From the aqueous extract | – | – | 24.9 |
| From the bicarbonate extract | 39.2 | 43.8 | 25.7 |
| From the alkaline and corresponding aqueous extract | 3.6 | 1.5 | 1.0 |

| | Yield of products upon dehydration of crude 1,3-diphenyl-(2′-naphthyl)-2-oxyglutaric acid, containing 53.1% pure acid, with a water-removing agent (%) | Yield of products upon dehydration of crude 1,3-(2′,2″-dinaphthyl)-2-phenyl-2-oxyglutaric acid, containing 40.3% pure acid, with a water-removing agent (in %) | Yield of products upon dehydration of crude 1,2,3-(2′,2″,2‴-trinaphthyl)-2-oxyglutaric acid, containing 15.4% pure acid, with a water-removing agent (in %) |
|---|---|---|---|
| From the neutral extract | 38.5 | 38.5 | 2.1 |

In sulfonating the monosulfonic acid (see Table 1), we obtained, in all probability, a mixture of fluorenones (10.1) and indones (30.0), which was again proved by means of the IR spectra of the corresponding crude products. The reason that oxyfluorenones are not obtained in larger amounts is probably their sulfonation to polysulfonic acids remaining in the sulfuric acid solution. Dehydration of this oxyglutaric acid with polyphosphoric acid likewise failed to give better results (see Table 1). If one assumes that here too the dehydration proceeds according to a scheme analogous to that for diphenylnaphthyl oxyglutaric acid, the formation of the following products should be expected: 4-(2′-naphthyl)-3-oxynaphtho-(2′,1′:1,2)-fluorenone and 4-(2″-naphthyl)-3-oxynaphtho-(3′,2′:1,2)-fluorenone, 2-(2′-naphthyl)-3-(2″-naphthylmethyl)-indone, and 1,3-(2′,2″-dinaphthyl)-2-phenylpropene.

Upon dehydration of 1,2,3-(2′,2″,2‴-trinaphthyl)-2-oxyglutaric acid with concentrated $H_2SO_4$ by the method already described, we isolated products whose yields are given in Table 1.

The monosulfonic acid was not desulfonated because of its small amount. From the resin obtained on acidification of the alkaline and corresponding aqueous extracts, we were unable to isolate crystals. In its IR spectrum a band at 1710 $cm^{-1}$ is visible, which is probably due to some fluorenone or to a mixture of fluorenones, and a band of a tertiary hydroxyl group at 3510 $cm^{-1}$. Thus, the resin contains some one of the isomers of 4-(2‴-naphthyl)-3-oxybenzonaphthofluorenone or a mixture of them. In the spectrum of the neutral resin there is a band characteristic of an indone and of a double bond. If it is assumed that dehydration of this oxyglutaric acid proceeds according to the scheme for diphenylnaphthyl oxyglutaric acid, the formation is possible of four naphthoxybenzonaphthofluorenones, of which, probably, chiefly 4-(2‴-naphthyl)-3-oxy-7,8-benzonaphtho-(2′,1′:1,2)-fluorenone is formed, since it arises as a result of $\alpha$-cyclization. By the same considerations, the indone is probably 2-(2‴-naphthyl)-3-(2″-naphthylmethyl)-6,7-benzindone, and the olefin

is 1,2,3-(2′,2″,2‴-trinaphthyl)-propene.

Here too, the reason for the low yields of oxybenzonaphthofluorenones is the same as in the preparation of dinaphthylphenyl oxyglutaric acid. Experiments on dehydration with polyphosphoric acid also did not give good results (see Table 1).

## Experimental Part

1. **Dehydration of 1,3-diphenyl-2-(2′-naphthyl)-2-oxyglutaric acid with conc. $H_2SO_4$.** To 1.9739 g of crude oxyglutaric acid* (containing 53.1% pure acid) is added

* By the method used by us, naphthyl-substituted oxyglutaric acids are obtained without purification from the corresponding arylsuccinic acids, and also from aromatic acids formed upon hydrolysis of the acid chloride used. Since

20 ml of 97% $H_2SO_4$. After 2 min the solution is poured into 250 ml of water. The mixture is extracted with ether. The ether extract is washed with water until the sample is no longer colored, then with bicarbonate solution until, upon acidification, it no longer becomes cloudy, and alternately with 2% NaOH and water until the ether solution is no longer colored blue-violet. From the aqueous solution, after addition of a large excess of $H_2SO_4$ and extraction with ether, 932.2 mg of a dark-red crystalline product is obtained; this is subjected to desulfurization. From the bicarbonate solutions, after acidification, 237.3 mg of carboxylic acids is extracted.

From the alkaline and corresponding aqueous solutions, upon acidification, 133.3 mg of a red-brown resin separates. From it, after chromatography on $Al_2O_3$, the following are obtained: from the colorless layer with benzene, 3.8 mg of oil; from the yellow zone with ether, 26 mg of resin. Crystals could not be obtained from these products. From the main red layer, with the aid of abs. alcohol, we extracted 66.7 mg of red-brown crystals, which, after successive recrystallization from *n*-butanol and benzene, give m.p. 214–214.5°.

| | |
|---|---|
| Found, %: | H 4.43; C 86.51 |
| $C_{27}H_{16}O_2$. Calculated, %: | H 4.33; C 87.07 |

From the neutral ether solution, 211.3 mg of a mixture of crystals and oil is obtained. From it, after chromatography on $Al_2O_3$, 39.5 mg of a crystalline product with m.p. 51–52° is separated from the colorless layer; from the yellow zone, 110.0 mg of benzyl-2-naphthyl ketone and 34 mg of resins, which do not crystallize.

**2. Desulfurization of the monosulfonic acid from experiment 1.** 932.2 mg of the monosulfonic acid is dissolved in 15 ml of water. To the solution is added 4.5 ml of 97% $H_2SO_4$ diluted with 7 ml of water. The mixture is placed in an autoclave and heated for 9 h at 200–208°. Extraction with ether is then

carried out. The ether solution is subsequently treated according to the procedure described in experiment 1. In this, 81.3 mg of carboxylic acids is isolated from the bicarbonate solution, and 232.6 mg of red resin from the alkaline and corresponding aqueous solutions; 52.4 mg of this is chromatographed on $Al_2O_3$. In all, 18.7 mg of oil and resin, which do not crystallize, is obtained; from the main red-orange layer, with the aid of a mixture of ether and alcohol, we extracted 32.1 mg of golden-yellow needle crystals, which, after recrystallization from *n*-butanol, melt at 273.5–274°.

| | |
|---|---|
| Found, %: | H 4.25; C 86.54 |
| $C_{27}H_{16}O_2$. Calculated, %: | H 4.33; C 87.07 |

From the neutral fractions, 377.6 mg of orange-red resin is obtained; 118.3 mg of the resin is chromatographed on $Al_2O_3$. In this, 58.5 mg of resin is extracted with benzene. After its dissolution in alcohol and slow crystallization, orange crystals with m.p. 162.5–163° are obtained.

| | |
|---|---|
| Found, %: | H 4.79; C 85.72 |
| $C_{26}H_{18}OC_2H_5OH$. Calculated, %: | H 4.89; C 85.69 |

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complete removal of these acids is very difficult, we used crude oxyglutaric acids, which we call crude. The content of pure oxyglutaric acid in them was determined by means of alkaline cleavage ([2]).

*Note: Figure translations are in progress. See original paper for figures.*

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