STUDIES ON MOLECULAR-REARRANGEMENTS OF α-GLYCOLS. VII.

RELATIVE ELECTRONEGATIVITIES OF β-NAPHTHYL AND DIPHENYLYL RADICALS.

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As for the dissociation degree of hexa-aryl ethanes, it is known that diphenylyl radical is more potent than phenyl, and naphthyl radicals are more potent than diphenylyl in causing the increase of dissociation of hexa-aryl ethanes. Thus, hexaphenyl ethane, tetraphenyl-bis-diphenylyl ethane, tetraphenyl-di-β-naphthyl ethane and tetraphenyl-di-α-naphthyl ethane dissociate into the corresponding monomers to 0%, 15%, 30% and 60% respectively.(1) According to the electronic conception of valency, instability of a carbon-to-carbon bond is attributed to the displacement of the binding electrons from one or both bound carbon atoms. Then, the increase of negativities of the substituents of a hexaaryl ethane will lead to the increase of dissociation of the ethane-molecule, since it causes the decrease of the negativities of the two adjacent carbon atoms in chain; in other word, it causes the increase of displacement of the binding electrons from the both carbon nuclei. Consequently, under certain conditions, it may be admitted to compare electronegativities of the substituents of hexa-aryl ethanes by their dissociation degree. Hereby, the above mentioned radicals will be in the following order with respect to their electronegativities: $\alpha\text{-}C_{10}H_7 > \beta\text{-}C_{10}H_7 > C_6H_5.C_6H_4 > C_6H_5$.

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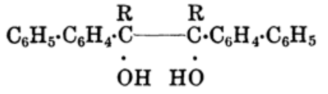
(1) Gomberg, *Chem. Rev.*, **1** (1925), 104.

In the recent papers dealing with the rearrangements of symmetrical aromatic pinacones, we can find some data concerning the migration tendency of diphenylyl radical with respect to some radicals in the pinacoline rearrangements (Table 1).

TABLE 1.

 $\underset{OH}{\overset{R}{C_6H_5 \cdot C_6H_4 \cdot C}}-\underset{HO}{\overset{R}{C}} \cdot C_6H_4 \cdot C_6H_5$	Migration aptitudes.		Observers.
R	$C_6H_5 \cdot C_6H_4$.	R.	
C_6H_5	96.5%.	4.5%.	Gomberg and Bachmann.[1]
p-BrC_6H_4	92.0%.	8.0%.	Gomberg and Bailar.[2]
p-$CH_3C_6H_4$	43%.	57%.	Bachmann and Moser.[3]
p-$CH_3OC_6H_4$	3.2%.	96.8%.	

It will be infered from these results that diphenylyl radical is by far more electropositive than p-anisyl radical, and slightly more positive than p-tolyl radical, but exceedingly electronegative than phenyl and p-bromophenyl radicals, since according to the author's theory,(4) the migratory tendencies of the substituents of a symmetrical pinacone can be taken for a criterion of their electronegativities.

In the present work, rearrangement of sym. di-β-naphthyl-bis-diphenylyl glycol has been studied, intending, on the one hand, to make a supplement to the series representing relative electronegativities of organic radicals by determining the relative positions of β-naphthyl and diphenylyl radicals in the series by the pinacoline method, and on the other hand, to check, thereby, the result infered from the dissociation degree of hexa-aryl ethanes.

On hydrolysing the rearrangement product of this pinacone, both β-naphthoic acid and p-phenyl-benzoic acid were obtained with slightly different yields, namely, the former with somewhat better yield than the latter. However, taking into consideration the remarkable difference in the easiness with which the two parent pinacolines are hydro-

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(1) Gomberg and Bachmann, *J. Am. Chem. Soc.*, **49** (1927), 251.

(2) Gomberg and Bailar, ibid., **51** (1929), 2237.

(3) Bachmann and Moser, ibid., **54** (1932), 1127.

(4) Migita, this Bulletin, **7** (1932), 341.

lysed (see p. 387), migration of β-naphthyl and diphenylyl radicals may be taken to occur nearly to an equal extent; in other words, there is no marked difference between these two radicals with respect to their electronegativities. Thus, the result obtained is not consistent with that infered from the dissociation degree of tetraphenyl-di-β-naphthyl and tetraphenyl-bis-diphenylyl ethanes. Though it can not be decided simply which of these results is more probable, the author wishes to place more weights upon the pinacoline method, since the hexa-aryl ethane method has often given deviated results,(1) probably owing to the fact that the dissociation degree of hexa-aryl ethanes depends not only on the negativities of substituents, but also on the experimental conditions, such as concentration, temperature and the solvent in which the dissociation takes place.

Sym. di-β-naphthyl-bis-diphenylyl glycol was prepared by reducing β-naphthyl-diphenylyl ketone with magnesium and magnesium iodide, while reduction of this ketone to the pinacone by other methods was proved unsuccessful.

Reduction of this ketone by zinc dust and glacial acetic acid is a subject of some interest, since it produced the corresponding methane at higher temperature, and the carbinol at room temperature.

The ketone remained unchanged by the action of alcohol under direct sunlight.

Experimental Part.

β-Naphthyl-Diphenylyl Ketone. β-$C_{10}H_7.CO.C_6H_4.C_6H_5$. This ketone was prepared from β-naphthoyl chloride and diphenyl by Friedel-Crafts' reaction, where the formation of the by-product, di-naphthoyl diphenyl, was avoided after Montagne's modification(2) employed in the prepara-of phenyl-diphenylyl ketone. 14.2 Gr. of the acid chloride and 12 gr. of aluminium chloride were warmed in 65 c.c. of carbon-bisulphide, to which were added, on cooling, 20 gr. of diphenyl (twice its equivalent quantity), and warmed on water bath. After twenty hours' heating, the aluminium complex was hydrolysed and the resulting yellowish-brown crystalline cakes were subjected to usual steam treatments. The raw products, after digestion with a small bulk of ether to remove coloured impurities, were crystallised from acetone with an addition of animal

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(1) For example, the dissociation degree of tetraphenyl-di-*p*-anisyl ethane is only about 30% (Gomberg and Buchler, *Chem. Rev.*, **1** (1925), 104), inspite of the presence of extremely negative anisyl radical.

(2) Montagne, *Rec. trav. chim.*, **27** (1908), 357.

charcoal. The ketone crystallised in slightly yellow scales with pearly lustre. A second recrystallisation from acetone gave practically colourless product melting at 136°C. which dissolves in concentrated sulphuric acid with orange colouration. The ketone is soluble in cold glacial acetic acid with an extreme difficulty, sparingly soluble in alcohol and ether, and readily soluble in benzene and hot acetone. The yield of the pure ketone amounted to about 40% of the theory.

Anal.: Subst. = 0.0784; CO_2 = 0.2566; H_2O = 0.0381 gr.
Found: C = 89.3; H = 5.45%.
Calc. for $C_{23}H_{16}O$ (Ketone): C = 89.6; H = 5.19%.

Reduction of the Ketone by Zinc Dust and Glacial Acetic Acid. (*a*) *At High Temperature.* 3 Gr. of the ketone were reduced by 6 gr. of zinc dust and 12 c.c. of glacial acetic acid with boiling. When the reaction product was poured into a large quantity of water, slightly yellow crystalline cakes were produced and the aqueous solution turned a white emulsion. The cakes were drained on porous plate and purified from hot ligroin. As yellowish viscid substance separated first from the hot solution, the upper solution was decanted and cooled effectively. White crystals, grouped in burr-like shape were deposited on the side of beaker, which melted at 106°C. after a second recrystallisation from ligroin, and dissolved in concentrated sulphuric acid with beautiful violet colour similar to that of the methyl-violets solution. Further purification from the same solvent did not improve the product. However, when recrystallised from glacial acetic acid, the product melted at 111°C. and dissolved in concentrated sulphuric acid to colourless solution. It was determined to be **β-naphthyl-diphenylyl methane** by elementary analysis and molecular weight determination. The yield of the pure compound was 30% of the theory.

Anal.: Subst. = 0.0706; CO_2 = 0.2418; H_2O = 0.0411 gr.
Found: C = 93.4; H = 6.68%.
Calc. for $C_{23}H_{18}$ (Naphthyl-diphenylyl methane): C = 93.9; H = 6.12%.

Mol. weight, measured after Rast. Subst. = 0.139; Camphor = 2.06 mgr.;
M. p. depress. = 9.0°C. Found: mol. weight = 300.
Calc. for $C_{23}H_{18}$ (Methane): mol. weight = 294.

It was proved that the violet colouration produced by the product melting at 106°C., when dissolved in concentrated sulphuric acid, was due to the corresponding carbinol contaminated as impurity, since the carbinol was formed by the reduction of the ketone with the same reagents but at room temperature, and it gave the same colouration when dissolved in concentrated sulphuric acid (See below).

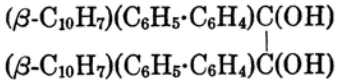
(*b*) *At Room Temperature.* One gram of the ketone, dissolved in sufficient glacial acetic acid (ca. 300 c.c.) to keep it in solution at room temperature, was reacted with excess of zinc dust for four days. The filtrate from unchanged zinc dust was poured into water, and the resulting white precipitates were drained on porous plate and purified from ligroin. The product forms white crystalline powder which melts at 118°C. to colourless liquid. It was proved to be **β-naphthyl-diphenylyl carbinol** from its composition and molecular weight. The yield was nearly quantitative.

Anal.: Subst. = 0.0636; CO_2 = 0.2065; H_2O = 0.0364 gr.
Found: C = 88.6; H = 6.41%.
Calc. for $C_{23}H_{18}O$ (Naphthyl-diphenylyl carbinol): C = 89.0; H = 5.81%.

Mol. weight, measured after Rast. Subst. = 0.240; Camphor = 2.05 mgr.;
M. p. depress. = 14.5°C. Found: mol. weight = 323.
Calc. for $C_{23}H_{18}O$ (Carbinol): mol. weight = 310.

The carbinol is readily soluble in most organic solvents, but with great difficulty in cold ligroin. It dissolves in concentrated sulphuric acid with colouration of intense violet, similar to that of methyl-violets solution.

Sym. Di-β-Naphthyl-bis-Diphenylyl Glycol,



$$\begin{array}{c}(\beta\text{-}C_{10}H_7)(C_6H_5\cdot C_6H_4)C(OH)\\ |\\ (\beta\text{-}C_{10}H_7)(C_6H_5\cdot C_6H_4)C(OH)\end{array}$$

Reduction of the Ketone by Magnesium and Magnesium Iodide. The reduction was carried out with 2 gr. iodine for magnesium iodide, 2 gr. of magnesium, 50 c.c. of ether-benzene and 2 gr. of β-naphthyl-diphenylyl ketone, just in the same way as in the case of di-*p*-methoxy-benzophenone.(1) On shaking lightly yellowish-green solution, the colour changed red and heat was evolved, while magnesium was coated with brownish sticky substance. After an hour or more, magnesium was uncoated, an intense bluish-green solution being obtained, which changed greyish-green in colour, on further shaking. At this point the solution was hydrolysed. The pinacone, after digestion with hot alcohol to take off unchanged ketone and then with ether to remove coloured impurities, was recrystallised from benzene. The purified product weighed 1.3 gr. which was 65% of the theoretical yield. It begins to decompose at 156°C. and melted to a yellow liquid at 163°C., which, when remelted, begins to sinter at 90°C. and melts to a clear liquid at 123°C. The pinacone does not dissolve in concentrated sulphuric acid,

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(1) This Bulletin, **7** (1932), 339.

while the sample, subjected to decomposition at melting point, dissolves in it with colouration of brownish-violet.

Anal.: Subst. = 0.0666; CO_2 = 0.2165; H_2O = 0.0356 gr.
Found: C = 88.6; H = 5.99%.
Calc. for $C_{46}H_{34}O_2$ (Pinacone): C = 89.3; H = 5.50%.

Rearrangement. 1.5 Gr. of this pinacone were boiled with the solution consisting of 20 c.c. of benzene, 10 c.c. of acetyl chloride, and 5 c.c. of acetic acid. The pinacone which was at first insoluble, gradually passed into solution with yellow colour, according as the rearrangement proceeded. After twelve hours' boiling the solvents were expelled under diminished pressure and the residue which formed yellow hard crusts was submitted to hydrolysis with 30 c.c. of 10% alcoholic potash. According with the progress of hydrolysis, white granular substance was observed depositing on the side of vessel. As the hydrolysis was found to require unexpectedly much of time, it was effected in two stages. After 48 hours' boiling, the alcoholic solution was decanted and the residue was extracted thrice with hot alcohol. The combined alcoholic solutions were analysed for organic acids, while the residue was boiled with a fresh addition of alcoholic potash for 240 hours.

Separation and identification of β-naphthoic acid and *p*-phenyl-benzoic acid in the presence of each other, were tried in various ways and were found to be hardly possible, though the individual acid has distinct properties (Table 2). Fortunately in the present case, these two acids appear in the different fractions of the hydrolysate, owing to a wide difference in facilities of scission of the two parent pinacolines.

Table 2.

	β-Naphthoic acid.	*p*-Phenyl-benzoic acid.
M. P.	182°C.	224°C.
Ag-salt.	Ag = 38.7%.	Ag = 35.4%.
Sublimate.	Feathery crystals.	Long silky fibres.
Thallo-salt.	Rosetted crystals.	Small diamond shaped crystals.
Ba-salt.	Needles with straight extinction, elongation negative.	Rhombs with diagonal extinction, elongation negative.

The acidic product in the first hydrolysate, when purified from ligroin with an addition of animal charcoal, crystallised in fine needles melting at 175°C., which was proved to be β-naphthoic acid contaminated with a minute quantity of *p*-phenyl-benzoic acid by the analysis of its silver salt. Microscopical examination of this product, however, failed to give the characteristic thallo-salt of β-naphthoic acid.

Anal.: Silver salt = 19.03; Ag = 7.41 mgr.
Found: Ag = 38.0%.
Calc. for silver naphthoate: Ag = 38.7%.

When this product was subjected to three successive crystallisations from ligroin, it melted at 182°C., sublimed in feathery crystals and gave the characteristic crystals of thallium- and barium salts under a microscope.

The acid obtained from the second hydrolysate, crystallised from ligroin in the forms of long white silky fibres, which melted at 224°C. and gave diamond shaped thallo-salt under microscope. Thereby, it was easily identified as *p*-phenyl-benzoic acid.

The yield of the crude β-naphthoic acid (m.p. 175°C.) amounted 0.04 gr. and that of *p*-phenyl-benzoic acid was nearly equal.

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