STUDIES ON MOLECULAR-REARRANGEMENTS OF α-GLYCOLS. VIII. REDUCTION OF αβ-DINAPHTHYL KETONE (AN ATTEMPT TO COMPARE THE ELECTRO-NEGATIVITIES OF α- AND β-NAPHTHYL RADICALS).

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Received December 3rd, 1932. Published January 28th, 1933.

Skraup⁽¹⁾ has observed in his research on the affinity requirement of organic radicals, that in the two naphthyl radicals, the affinity requirement in α-position is stronger than in β-position.

In the studies on dissociation of hexa-aryl ethanes, Gomberg and his colaborators⁽²⁾ have found that α-naphthyl radical is more potent than β-naphthyl radical, in causing the dissociation of the ethane-molecules, e.g. di-α-naphthyl-tetraphenyl ethane dissociates into the monomer to 68% in benzene solution, while di-β-naphthyl-tetraphenyl ethane dissociates to 32.3%. If it is admitted to take the dissociation degree of hexa-aryl ethanes for a criterion of electronegativities of substituents in their molecules⁽³⁾, we can infer from these results that between α- and β-naphthyl radicals the former exceeds the latter in its electronegativity.

The author⁽⁴⁾ has attained to the same result, infering the relative electronegativities of α- and β-naphthyl radicals indirectly from the fact

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(1) Skraup, *Ber.*, **55** (1922), 1080.
(2) Gomberg, *Chem. Rev.*, **1** (1925), 104.
(3) Migita, this Bulletin, **7** (1932), 382.
(4) Migita, this Bulletin, **7** (1932), 378.

that in the rearrangement of sym. di-*p*-anisyl-di-*α*-naphthyl glycol⁽⁵⁾, *α*-naphthyl radical migrates, though to a lesser extent, as well as *p*-anisyl radical, while in the case of sym. di-*p*-anisyl-di-*β*-naphthyl glycol, migration of *p*-anisyl radical occurs almost exclusively.

Though it is intended, in the present work, to compare the electronegativities of *α*- and *β*-naphthyl radicals directly by the pinacoline method from the rearrangement products of sym. *ααββ*-tetranaphthyl glycol, all attempts to obtain this pinacone from *αβ*-dinaphthyl ketone have proved unsuccessful.

Glacial acetic acid and zinc dust reduced this ketone to *αβ*-dinaphthyl methane at higher temperature, and to *αβ*-dinaphthyl carbinol at room temperature, as in the case of *β*-naphthyl-diphenylyl ketone⁽⁶⁾. The author has also proved that the similar result is obtained under the same conditions in the case of *α*-naphthyl-diphenylyl ketone. The formation of the corresponding methanes in the reduction of ketones by *zinc dust and glacial acetic acid* is considered to be rather anomalous, and the case of Michler's ketone⁽⁷⁾ is probably the only precedent found in literature.

In this anomalous reduction, negativities of the substituents are not deemed to be the directing factor, because ketones containing more negative radicals than naphthyl are not reduced to the methanes under the same conditions, as seen in the case of di-*p*-methoxy-benzophenone⁽⁸⁾ and *p*-methoxy-*p*′-ethoxy-benzophenone⁽⁸⁾. The author wishes to attribute this to the sterical influence of the substituents. The fact that Michler's ketone (I) is reduced to corresponding methane by zinc dust and acetic acid, while dimethyl-*p*-aminobenzophenone⁽⁹⁾ (II) is reduced to corresponding pinacone, seems to throw some hints on this problem.

$$\text{(I)}\quad (CH_3)_2NC_6H_4\cdot CO\cdot C_6H_4N(CH_3)_2\,,\qquad \text{(II)}\quad (CH_3)_2NC_6H_4\cdot CO\cdot C_6H_4NH_2\,.$$

αβ-Dinaphthyl ketone remained unchanged by the action of absolute alcohol under direct sunlight, as in the case of *p*-anisyl-*β*-naphthyl ketone, presumably owing to its extremely small solubility in absolute alcohol.

When the ketone was reduced by magnesium and magnesium iodide, the reaction seemed to proceed for the desired direction, since evolution of heat and formation of ketyl solution with wine-colour were observed in the process of reduction. However, the reaction product was dark

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(5) Bailar, *J. Am. Chem. Soc.*, **52** (1930), 3596–3603.
(6) Migita, this Bulletin, **7** (1932), 385–386.
(7) Votoček and Krauz, *Ber.*, **42** (1909), 1602.
(8) Migita, this Bulletin, **7** (1932), 335, 342.
(9) Willstätter and Goldmann, *Ber.*, **39** (1906), 3768.

coloured rosinous matter, of which purification from organic solvents was tried in vain by every means. On allowing the syrupy product to stand at room temperature for a long period, a minute quantity of granular crystals was obtained. But the yield was too poor to give a further investigation.

Experimental Part.

αβ-Dinaphthyl Ketone. This ketone was prepared after Tschitschibabin and Korjagin(10), from 30 gr. of α-bromo-naphthalene, 4 gr. of magnesium and 15 gr. of β-naphtho-nitrile. The product, purified from acetic ester, melts at 136–7°C. It dissolves in concentrated sulphuric acid with orange colour.

Reduction of αβ-Dinaphthyl Ketone.

Reduction by Zinc Dust and Glacial Acetic Acid. (a) *At Boiling Temperature.* Two grams of the ketone were reduced by boiling with 8 c.c. of glacial acetic acid and 4 gr. of zinc dust, and the reaction product was usually poured into water. The resulting precipitates contained yellowish substance which is readily soluble in organic solvents imparting the solution green fluorescence, and were found freed from it only by repeated fractional crystallisation from hot ligroin. As this impurity separates out as yellowish rosinous matter from warm ligroin solution, the crude product was dissolved in hot ligroin and the solution was decanted from the rosin after full precipitation of it, and cooled quietly. White crystalline mass which deposited on the side of beaker, was gathered and recrystallised from ether. It forms thick prisms and melts at 96°C. It was identified by this melting point and elementary analysis as αβ-dinaphthyl methane, prepared by Tschitschibabin(11) by reducing αβ-dinaphthyl carbinol with hydrogen iodide in hot glacial acetic acid.

Anal.: Subst. = 0.0712; CO_2 = 0.2440; H_2O = 0.0396 gr.
Found: C = 93.6; H = 6.24%.
Calc. for $C_{21}H_{16}$ (αβ-dinaphthyl methane): C = 94.0; H = 5.97%.

(b) *At Room Temperature.* To the solution of 2.2 gr. of the ketone dissolved in sufficient glacial acetic acid (ca. 400 c.c.) to keep it solution at room temperature, were added 10 gr. of zinc dust, and the reaction mixture was allowed to stand at room temperature for five days. The crude product, obtained after usual treatments, was found readily

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(10) Tschitschibabin and Korjagin, *Chem. Centr.*, (1914), I, 1658.

(11) Tschitschibabin, *Ber.*, **44** (1911), 449.

soluble in organic solvents except ligroin and petroleum ether. It crystallises from a quantity of ligroin in fine white needles, grouped in burr-like masses, which melts at 112–3°C. to a colourless liquid⁽¹²⁾. It dissolves in concentrated sulphuric acid with pure blue colour. It was identified from these properties and the elementary analysis, as αβ-dinaphthyl carbinol, prepared by Tschitschibabin⁽¹³⁾ from α-bromo-naphthalene and β-naphthaldehyde by Grignard's reaction. The yield was nearly quantitative.

Anal.: Subst. = 0.0684; CO_2 = 0.2219; H_2O = 0.0347 gr.
Found: C = 88.6; H = 5.70%.
Calc. for $C_{21}H_{16}O$ (αβ-dinaphthyl carbinol): C = 88.7; H = 5.64%.

Reduction by Absolute Alcohol under Direct Sunlight. Two grams of ketone and 50 c.c. of absolute alcohol were sealed in a tube and exposed to direct sunlight for about two months. Though the weather was not favourable, the net time of exposure amounted to 200 hours. During the exposure, the solution assumed brownish tint, but on opening the tube, formation of acetaldehyde was not observed and the crystals in the tube were identified as unchanged ketone which was recovered quantitatively.

Reduction by Magnesium and Magnesium Iodide. To 2 gr. of powdered magnesium, suspended in 20 c.c. ether and 30 c.c. of benzene were added 2 gr. of iodine and kept the solution boiling quite vigorously. The practically colourless solution of the magnesium iodide was cooled and to it were added 2 gr. of αβ-dinaphthyl ketone dissolved in 10 c.c. of benzene. While the reaction mixture was shaken, heat was evolved and after few hours the solution assumed wine-colour. Shaking was continued until evolution of heat ceased and magnesium was uncoated. After twenty hours, the green solution was filtered from unchanged magnesium and was hydrolysed by dilute sulphuric acid with the addition of a pinch of sodium bisulphite. The benzene solution was dehydrated with sodium sulphate and the solvent was distilled off. Brown syrupy residue was easily soluble in organic solvents and purification from various organic solvents has been tried in vain. On allowing the syrupy mass to stand for about two weeks, some crystals were deposited on the side of beaker, which dissolved in concentrated sulphuric acid with intense green colouration. However, the yield was too poor to give a further investigation.

p-Bromo-Diphenyl. p-Bromo-diphenyl was prepared after Gomberg and Bachmann⁽¹⁴⁾ by diazotizing p-bromo-aniline and coupling it with benzene. Purification of the crude product was, however, simplified by

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(12) Tschitschibabin purified this carbinol from benzene and gave it a melting point 106–7°C. However, his sample is probably not in a reliably pure state, since benzene, in which this carbinol is rather easily soluble, is not taken for a suitable solvent for purification. The author has actually observed that the carbinol obtained by purifying the crude product from benzene, melted at 106–7°C. *to a yellow liquid,* while the product purified from ligroin melted at 112–3°C. *to a colourless liquid.*

(13) Tschitschibabin, *Ber.*, **44** (1911), 447.

(14) Gomberg and Bachmann, *J. Am. Chem. Soc.*, **46** (1924), 2339.

recrystallising it from hot ligroin with an addition of animal charcoal. It crystallises in white lamellar, melting 90–91°C. to colourless liquid, while the product purified by the original method(15), melted to slightly coloured liquid at 89–90°C.

α-Naphthyl-Diphenylyl-Ketone. This ketone was prepared from 14.4 gr. of *p*-bromo-diphenyl, 0.5 gr. of activated magnesium and 10 gr. of α-naphtho-nitrile. The resulting magnesium complex was hydrolysed and subjected to steam distillation alternately in acidic and alkaline reactions. Dark coloured product was treated with ether to remove colouring impurities, and then purified from a quantity of absolute alcohol. It crystallises in fine needles, melting at 140–141°C. It is sparingly soluble in cold organic solvents, especially in glacial acetic acid. It dissolves in concentrated sulphuric acid with reddish orange colouration. The yield of the purified product was about 3.5 gr.

Anal.: Subst. = 0.0627; CO_2 = 0.2055; H_2O = 0.0301 gr.
Found: C = 89.4; H = 5.38%.
Calc. for $C_{23}H_{16}O$ (α-naphthyl-diphenylyl-ketone): C = 89.6; H = 5.19%.

α-Naphthyl-Diphenylyl-Carbinol, $(\alpha\text{-}C_{10}H_7)(C_6H_5.C_6H_4)CHOH$. One gram of α-naphthyl-diphenylyl ketone was dissolved in 300 c.c. of glacial acetic acid and was allowed to react with excess of zinc dust for four days at 25°C. The reaction mixture was treated as usual and the resulting raw product was recrystallised from ligroin. It crystallises in white microscopical prisms, melting at 131°C. to a glassy mass. It dissolves in concentrated sulphuric acid imparing the solution intense greenish blue colour. Its composition was found corresponding to carbinol or pinacone, but it was identified as the carbinol from the facts that the product gives the same colouration toward concentrated sulphuric acid, before and after fusion, and that the original ketone is reduced to corresponding methane by the same reducing agents but at the boiling temperature of the reacting mixture (See below).

Anal.: Subst. = 0.0649; CO_2 = 0.2107; H_2O = 0.0339 gr.
Found: C = 88.5; H = 5.86%.
Calc. for $C_{23}H_{18}O$ (α-naphthyl-diphenylyl carbinol): C = 89.0; H = 5.81%.

The yield was practically quantitative.

α-Naphthyl-Diphenylyl-Methane, $(\alpha\text{-}C_{10}H_7)(C_6H_5.C_6H_4)CH_2$. α-Naphthyl-diphenylyl ketone was usually reduced in gently boiling glacial

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(15) Alcoholic solution of the raw product was decolourized by zinc dust and concentrated hydrochloric acid. The solution was filtered and allowed to crystallise.

acetic acid solution with zinc dust. On pouring the reaction product into water, yellowish crystalline cakes separated and the solution turned milky. The precipitates were recrystallised twice from glacial acetic acid and finally from ligroin with an addition of animal charcoal. It crystallises in thick prisms, melting at 146°C. Purified product does not dissolve in concentrated sulphuric acid, while raw product gives greenish blue colouration toward it. This colouration is due to the presence of a small quantity of the carbinol, which is removed only by recrystallising from glacial acetic acid. The product was proved to be the corresponding methane, α-naphthyl-diphenylyl methane, from its composition and molecular weight. The yield of the pure product did not exceed 40% of the theory.

Anal.: Subst. = 0.0635; CO_2 = 0.2177; H_2O = 0.0365 gr.
Found: C = 93.5; H = 6.41%.
Calc. for $C_{23}H_{18}$ (α-naphthyl-diphenylyl-methane): C = 93.9; H = 6.10%.
Mole. weight: Subst. = 0.270; Camphor = 2.834 mgr.
Depres. of m.p. = 13.0°C.
Found: Mole. weight = 294. Calc. for $C_{23}H_{18}$: Mole. weight = 294.

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