STUDIES ON MOLECULAR-REARRANGEMENTS OF α-GLYCOLS. VI.
RELATIVE ELECTRONEGATIVITIES OF p-ANISYL AND NAPHTHYL RADICALS.

By Masao MIGITA.

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In the earlier literatures naphthyl radicals are conceived to be the most electronegative radicals. Thus Skraup⁽¹⁾ has obtained the result that naphthyl radicals have the highest "affinity requirement" and p-anisyl radical is next to them, when he has compared so called affinity requirement of organic radicals by his "oxazol-" and "carbinol-" methods. It has been already discussed that the "affinity requirement" is nothing but electronegativity.⁽²⁾

Establishing the relative electronegativities of organic radicals by double decomposition of unsymmetrical organomercuric compounds and hydrogen chloride, Kharasch and Marker⁽³⁾ have given the result that naphthyl radicals rank first and p-anisyl radical comes next. But later, after closer experiments, the following correction was made for this order that p-anisyl radical is the most negative and α-naphthyl radical is the second.⁽⁴⁾

It will be interesting to check these results by determining the relative electronegativities of p-anisyl and naphthyl radicals by some other method. For this purpose, we can find an excellent method in the rearrangements of symmetrical pinacones, which has been proposed by the author with its theoretical deduction, and its applicability has been proved by a series of experimental data.⁽⁵⁾

As for α-naphthyl radical, Bailar⁽⁶⁾ calculated its migration tendency with respect to p-tolyl and p-anisyl radicals, in the rearrangements of sym. di-p-tolyl-di-α-naphthyl glycol and sym. di-p-anisyl-di-α-naphthyl glycol, and found that taking the migration tendency of α-naphthyl radical 1, those of p-tolyl and p-anisyl radicals are 0.88 and 2 respectively. This Bailar's result can be interpreted from the author's theory as follows: α-naphthyl

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(1) Skraup, *Ber.*, **55** (1919), 1080, 1074.

(2) Migita, this Bulletin, **7** (1932), 342 foot-note.

(3) Kharasch and Marker, *J. Am. Chem. Soc.*, **48** (1926), 3130.

(4) Kharasch and Reinmuth, *J. Chem. Education*, **5** (1928), 408.

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

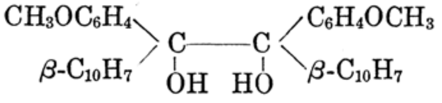
(6) Bailar, *J. Am. Chem, Soc.*, **52** (1930), 3596–3603.

radical is somewhat more negative than *p*-tolyl radical and fairly more positive than *p*-anisyl radical.

As little has been known of electronegativity of β-naphthyl radical, intending to determine the rank of this radical in the series representing relative electronegativities of organic radicals by the pinacoline method, the rearrangement of sym. di-*p*-anisyl-di-β-naphthyl glycol (I) was first studied.

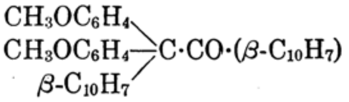
In the actual rearrangement of this glycol (I) migration of anisyl radical takes place exclusively, di-*p*-anisyl-β-naphthyl-β-naphthoyl methane (II) being produced, which shows that *p*-anisyl is by far more negative than β-naphthyl radical, conforming with the result given by Kharasch and Reinmuth in the later paper.

(I)



$$(CH_3OC_6H_4)(\beta\text{-}C_{10}H_7)C(OH)\text{—}C(OH)(C_6H_4OCH_3)(\beta\text{-}C_{10}H_7)$$

(II)



$$(CH_3OC_6H_4)_2(\beta\text{-}C_{10}H_7)C\cdot CO\cdot(\beta\text{-}C_{10}H_7)$$

It is interesting that migration of α-naphthyl radical takes place, though to a lesser extent, as well as *p*-anisyl radical, in the rearrangement of sym. di-*p*-anisyl-di-α-naphthyl glycol, while in the case of sym. di-*p*-anisyl-di-β-naphthyl glycol, migration of *p*-anisyl radical nearly exclusively occurs. Because these results lead us to the inference that α-naphthyl is more negative than β-napthyl radical, since in the rearrangement of a symmetrical pinacone, the two substituents migrate with different aptitudes, namely, the more negative radical has the greater migratory aptitude, and migration of one radical takes place exclusively, when the electronegativities of the two substituents are widely different, as discussed in the last paper.⁽¹⁾

Sym. di-*p*-anisyl-di-β-naphthyl glycol is obtained by reducing *p*-anisyl-β-naphthyl ketone by glacial acetic acid and zinc dust at room temperature. The corresponding pinacoline (II) is obtained by the action of acetyl chloride on the pinacone or simply by heating the pinacone with acetic acid. Therefore, the reduction of the ketone by glacial acetic acid and zinc dust at higher temperature gives the pinacoline as in the case of di-anisyl ketone and *p*-methoxy-*p'*-ethoxy-benzo-phenone.⁽²⁾ Here we can find another instance of increase of reactivity of a pinacone caused by highly negative substituents in the molecule.

When *p*-anisyl-β-naphthyl ketone was reduced by absolute alcohol under direct sunlight, change of its crystalline form was observed from thick prisms to thin leaflets, but the ketone remained unchanged.

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(1) Loc. cit.

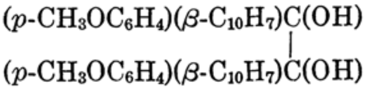
(2) Migita, this Bulletin, **7** (1932), 338, 343.

Experimental Part.

p-Anisyl-β-Naphthyl Ketone, $p\text{-}CH_3OC_6H_4\cdot CO\cdot\beta\text{-}C_{10}H_7$. The ketone was prepared from β-naphthoyl chloride (19.0 gr.) and anisole (12 gr.) by Friedel-Crafts' reaction. The reaction proceeded smoothly and after usual steam treatment, dark coloured buttery mass was obtained which could be purified either from hot ligroin or hot alcohol. From ligroin it crystallised in an aggregate of slightly coloured prisms, while from the latter it crystallised in white scales with pearly lustre. When recrystallised from alcohol, it crystallises in scales or needles depending on conditions and melts at 93°C. It dissolves in concentrated sulphuric acid with orange colour. The yield of the pure product amounted to 14 gr. which represents 54 % of the theory.

Anal.: Subst. = 0.0685; CO_2 = 0.2067; H_2O = 0.0342 gr.
Found: C = 82.3; H = 5.59%.
Calc. for $C_{18}H_{14}O_2$ (Ketone): C = 82.5; H = 5.59%.

Sym. Di-p-Anisyl-di-β-Naphthyl Glycol,



$$\begin{array}{l}(p\text{-}CH_3OC_6H_4)(\beta\text{-}C_{10}H_7)C(OH)\\ \qquad\qquad\qquad\qquad\quad |\\ (p\text{-}CH_3OC_6H_4)(\beta\text{-}C_{10}H_7)C(OH)\end{array}$$

2.3 Gr. of p-anisyl-β-naphthyl ketone were dissolved in sufficient glacial acetic acid (ca. 50 c.c.) to keep it in solution at room temperature, to which 10 gr. of zinc dust were added, allowing the mixture to stand at room temperature for five days. White precipitates which fell over zinc dust, were filtered, boiled with ether to remove impurities and finally recrystallised from benzene and petroleum ether. It melts at 160°C., and dissolves in concentrated sulphuric acid with dark brown colouration which assumes gradually reddish tint. It is almost insoluble in alcohol and ether. The yield was about 0.5 gr. By boiling the unchanged zinc dust with benzene, a further quantity of the glycol was obtained.

Anal.: Subst. = 0.0634; CO_2 = 0.1906; H_2O = 0.0345 gr.
Found: C = 82.1; H = 6.11%.
Calc. for $C_{36}H_{30}O_4$ (Pinacone): C = 82.2; H = 5.71%.

When the acetic acid solution from which the pinacone and unchanged zinc dust were filtered off, was poured into water, white precipitates were obtained, which, however, when purified from benzene and petroleum ether, produced only syrupy substance, which dissolves in organic solvent with yellow colour.

Rearrangement. The pinacone was boiled with acetic acid for 10 minutes and poured into water. Resulting white flocculent precipitates were recrystallised from ether. The product melts at 185°C. with frothing. No depression of melting point was observed, when mixed with di-*p*-anisyl-β-naphthyl-β-naphthoyl-methane, prepared by reducing the ketone with boiling acetic acid and zinc dust (See below). The yield was nearly quantitative.

By treating the pinacone with acetyl chloride and glacial acetic acid in benzene solution, the same result was obtained.

Di-*p*-Anisyl-β-Naphthyl-β-Naphthoyl-Methane,

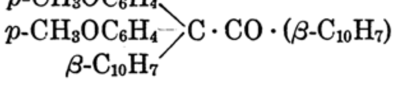
$(\beta\text{-}C_{10}H_7)(p\text{-}CH_3OC_6H_4)_2C.\,CO.\,\beta\text{-}C_{10}H_7.$

To gently boiling solution of *p*-anisyl-β-naphthyl ketone (5.2 gr.) in glacial acetic acid (24 c.c.), 12 gr. of zinc dust were added by portions. Slightly yellowish precipitates which were obtained by pouring the reaction products into water, were drained and dissolved in ether. When this etheral solution was boiled gently, white crystalline powder gradually precipitated, being freed from impurities which remained in solution. The product, purified from chloroform and ether, melts at 185°C. with frothing. It is nearly insoluble in ether, only sparingly in hot ligroin and alcohol, readily soluble in chloroform, acetic acid and hot benzene. It dissolves in concentrated sulphuric acid with brownish black colour, which assumes gradually reddish tint.

Anal.: Subst. = 0.0754; CO_2 = 0.2346; H_2O = 0.0387 gr.
Fonnd: C = 84.8; H = 5.75%.
Calc. for $C_{36}H_{28}O_3$ (Pinacoline): C = 85.1; H = 5.51%.

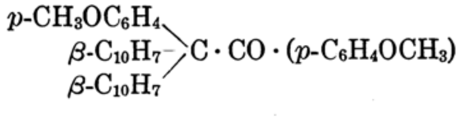
Constitution. The constitution of this pinacoline is either of the two possible isomers, II and III, which give, by hydrolysis, β-naphthoic acid and *p*-anisic acid respectively.

(II)



$$\left.\begin{array}{r} p\text{-}CH_3OC_6H_4 \\ p\text{-}CH_3OC_6H_4 \\ \beta\text{-}C_{10}H_7 \end{array}\right\rangle C\cdot CO\cdot(\beta\text{-}C_{10}H_7)$$

(III)



$$\left.\begin{array}{r} p\text{-}CH_3OC_6H_4 \\ \beta\text{-}C_{10}H_7 \\ \beta\text{-}C_{10}H_7 \end{array}\right\rangle C\cdot CO\cdot(p\text{-}C_6H_4OCH_3)$$

Though these two acids have close melting points, they can be easily distinguished by their solubilities in water and in ligroin and by the optical properties of the crystals (See the following table).

	β-Naphthoic acid.	*p*-Anisic acid.
M. P.	184°C.	182°C.
Optical properties.	Monoclinic prisms, elongation positive for crystals with straight extinction.	Monoclinic prisms, elongation negative for crystals with straight extinction.
Solubility in hot water.	Very difficultly.	Moderately.
Solubility in hot ligroin.	Recrystallisable.	Only in trace.

2 Gr. of the pinacoline were boiled with 100 c.c. of 20% alcoholic potash. The pinacoline which is insoluble in hot alcohol, passed gradually into solution as the hydrolysis proceeded. After about twenty hours a clear solution was obtained, which, however, was kept boiling further for six hours. Alcohol was expelled under reduced pressure, acidic and neutral constituents being isolated by usual method.(1)

The acidic product which was insoluble in hot water, was dissolved in a quantity of hot ligroin. On cooling the solution, it was obtained in the form of slightly coloured fine needles, which were recrystallised from ligroin with an addition of animal charcoal. It melted at 184°C., and was identified as β-naphthoic acid by mixed melting point test and by the optical properties of the crystals.

The neutral constituent was obtained as dark coloured syrup which was deemed impossible to be brought into crystallisation. However, the author has succeeded in obtaining thick prisms by leaving it to stand at room temperature for two months. The crystals, purified with ether on porous plate, melted at 89–90°C. with frothing and solidified in a glassy mass. Its composition was coincident with that of di-*p*-anisyl-β-naphthyl-methane, $(p\text{-}CH_3OC_6H_4)_2CH(\beta\text{-}C_{10}H_7)$.

Anal.: Subst. = 0.0648; CO_2 = 0.2010; H_2O = 0.0385 gr.
Found: C = 84.6; H = 6.63%.
Calc. for $C_{25}H_{22}O_2$: C = 84.7; H = 6.21%.

Thus it has been proved that in the rearrangement of sym. di-*p*-anisyl-di-β-naphthyl glycol, migration of *p*-anisyl radical took place exclusively and the pinacoline, produced, has the constitution of formula II.

Reduction by Absolute Alcohol under Direct Sunlight. Two grams of *p*-anisyl-β-naphthyl ketone were sealed in a tube with about 50 c.c. of

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(1) Migita, this Bulletin, **7** (1932), 344.

absolute alcohol and exposed to direct sunlight for a month. After the end of the first week, change of crystalline form was observed from thick prisms to thin leaflets. On opening the tube, however, formation of acetaldehyde was detected neither by smell nor by Schiff's reagent. The leaflets were filtered and recrystallised from alcohol. It melted at 93°C. and dissolved in concentrated sulphuric acid with orange colour. It was identified as the original ketone by mixed melting point test.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.