STUDIES ON MOLECULAR-REARRANGEMENTS OF α-GLYCOLS. V. RELATIVE ELECTRONEGATIVITIES OF *p*-METHOXY-PHENYL AND *p*-ETHOXY-PHENYL RADICALS.

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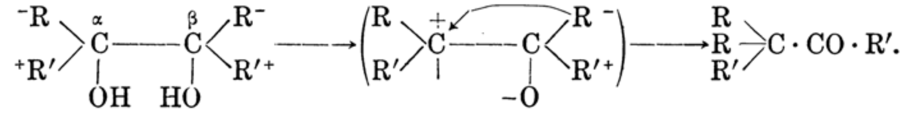
The author has observed that tetra-*p*-methoxybenzopinacone shows extreme facility to undergo molecular rearrangement and has attributed this behaviour to accumulation of strongly negative substituents in the molecule.⑴ In order to confirm this assumption by another example on the one hand, and to compare relative electronegativities of *p*-methoxyphenyl and *p*-ethoxyphenyl radicals on the other hand, the reduction of 4-methoxy-4′-ethoxy-benzophenone and the rearrangement of the corresponding pinacone are studied. The principle of the determination of relative electronegativities of organic radicals by pinacoline rearrangement is based on the fact that in the rearrangement of *symmetrical* pinacone, $RR'C(OH)\cdot C(OH)RR'$, migration of the more negative radical, say R, takes place principally, and pinacoline $RRR'\ C\cdot CO\cdot R'$ is the chief product.⑵ This selective migration of the substituents in the rearrangement of a symmetrical pinacone can be interpreted as follows:



The α carbon atom in the fraction of molecule, $RR'\underset{\bullet}{C}\cdot C\underset{\bullet}{O}\cdot RR'$, which is assumed to be produced intermediately, is highly negatively polarized, since this carbon atom has been deprived of a part of its bond-forming electrons with the elimination of hydroxyl group. Therefore, if a radical migrates to this carbon atom from the other, the more negative radical is naturally assumed to wander with greater easiness.

As for the relative electronegativities of lower alkyl radicals, the results given by different methods are not concordant, but it is generally accepted that no parallelism exists between electronegativities of alkyl

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(1) Migita, this Bulletin, **7** (1932), 336.

(2) We can find a series of such cases in literature, for example, $R = C_6H_5$, $R' = CH_3$; $R = CH_3OC_6H_4$, $R' = C_6H_5$; $R = C_6H_5C_6H_4$, $R' = C_6H_5$.

radicals and the number of their carbon atoms and that methyl radical is more electronegative than ethyl.(1)

Now, if methyl radical is more negative than ethyl, in the case of alkoxy-radicals the relation of negativities will be inversed by the theory of induced polarity, ethoxy being more negative than methoxy radical. Nextly when this methoxy or ethoxy radical enters in phenyl radical at para position, the relation of electronegativities between these alkoxyphenyl radicals are the same with that between the original alkoxy radicals, since the effect of the negativities of alkoxy radicals appear alternately in the carbon atoms of the benzene ring. Thus *p*-ethoxyphenyl will be more negative than *p*-methoxy radical.

Now, in the actual rearrangement of sym. dimethoxy-diethoxybenzopinacone, migration of ethoxy radical took place almost exclusively and 4-methoxyphenyl-bis(4′-ethoxyphenyl)-4″-methoxybenzoyl-methane, $(C_2H_5OC_6H_4)_2(CH_3OC_6H_4)C.CO.C_6H_4OCH_3$ was produced. This shows, as expected, that *p*-ethoxyphenyl radical is more negative than *p*-methoxyphenyl, and thereby, it gives an indirect proof on the more negative character of methyl radical than ethyl.

On reduction by glacial acetic acid and zinc dust, 4-methoxy-4′-ethoxybenzophenone gives corresponding pinacoline, as in the case of dimethoxybenzophenone. This is to be expected, as both the ketones are accumulated with highly negative radicals.

It is highly interesting that a fair quantity of the pinacoline, but no pinacone, was isolated from reduction products of this ketone by absolute alcohol under direct sunlight, while in the case of dimethoxybenzophenone, pinacone was the only product. It is inferable, thereby, that between these two substituted benzophenones the former exceeds the latter in its reactivity, which is consistent with the fact that *p*-ethoxyphenyl is more negative than *p*-methoxyphenyl radical, since the reactivity of a pinacone is considered to increase according as the negativities of substituents are raised.(2) As for the mechanism of pinacoline formation by this reduction, it was assumed if a minute quantity of

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(1) $C_3H_7 > CH_3 > C_2H_5$, by carbinol method (Skraup, *Ber.*, **55** (1922), 1074).
$CH_3 > C_3H_7 > C_2H_5$, by pinacoline method (Meerwein, *Ann.* **419** (1919), 121.)
$CH_3 > C_2H_5 > C_3H_7$, by dialkylmercury method (Kharasch and Marker, *J. Am. Chem. Soc.*, **48** (1926), 3130).

Skraup and Meerwein did not use the term "electronegativity," but employed the term "affinity requirement." These two expressions, however, are the same in essence, since "affinity requirement" can be understood from electronic conception of valency as affinity for binding electrons.

(2) Migita, this Bulletin, **7** (1932), 336.

acetic acid was produced by oxidation of alcohol, and if this alcoholic acetic acid behaved as rearranging agent. This assumption, however, was given up for the actual reduction products did not give acidic reaction.

Experimental Part.

4-Methoxy-4′-Ethoxy-Benzophenone, $CH_3OC_6H_4.CO.C_6H_4OC_2H_5$. *p*-Anisoyl chloride, prepared from 15 gr. of *p*-anisic acid and a slight excess of thionyl chloride, was reacted in the presence of 12 gr. of aluminium chloride with 13 gr. of phenetol in carbon bisulphide solution. The reaction proceeded very smoothly and completed in few hours. On hydrolysing the aluminium complex, dark brownish heavy oil was obtained, which solidified in buttery mass by repeated steam distillation alternately in very weak acid and alkaline reactions. From hot alcoholic extract of this buttery mass 4-methoxy-4′-ethoxy-benzophenone crystallised out in scales with pearly lustre, which were drained on porous plate. Recrystallised methoxy-ethoxy-benzophenone melts at 106–107°C., is readily soluble in hot ligroin and cold ether, and difficultly in cold alcohol and acetic acid. When recrystallised from ligroin, the ketone precipitates in gelatinous mass. It dissolves in concentrated sulphuric acid with yellow colour.

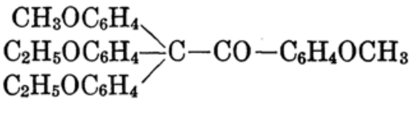
Anal.: Subst. $= 0.0742$; $CO_2 = 0.2030$; $H_2O = 0.0415$ gr.
Found: $C = 74.7$; $H = 6.22\%$. Calc. for $C_{16}H_{16}O_3$ (Ketone): $C = 75.0$; $H = 6.26\%$.

4-Methoxyphenyl-bis (4′-Ethoxyphenyl)-4″-Methoxybenzoyl-Methane, $(CH_3OC_6H_4)(C_2H_5OC_6H_4)_2C.CO.C_6H_4OCH_3$. (a) *Reduction by Hot Acetic Acid and Zinc Dust.* Three grams of zinc dust were added in portions to gently boiling solution of 1.35 gr. methoxyethoxybenzophenone in 6 c.c. acetic acid. After four hours' boiling, acetic acid solution, filtered from unchanged zinc dust, was poured into a large quantity of water, pale yellowish flocculent precipitates being obtained. The unchanged zinc dust was treated twice with hot acetic acid and the combined extracts were treated in the same way. The crude product was readily soluble in ether, but in the solution it became free from yellow impurities and the ketone separated out as colourless granular crystals. Purifications from other solvents could not bring desired results. It melts at 160°C. and solidifies vitreously. It is readily soluble in benzene, and moderately in hot ligroin but sparingly in cold. It dissolves in concentrated sulphuric acid with dark brown colour which changes to intense bluish purple. The product was found, by analysis, to be the corresponding pinacoline, but not the pinacone.

Anal.: Subst. = 0.0696; CO_2 = 0.1970; H_2O = 0.0415 gr.
Found: C = 77.2; H = 6.61%.
Calc. for $C_{32}H_{32}O_5$ (Pinacoline): C = 77.5; H = 6.45%.

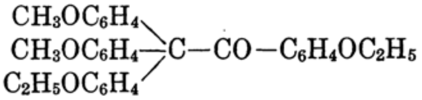
Constitution. By reduction of methoxyethoxybenzophenone, we may have two isomeric pinacolines, I and II, which will give on hydrolysis with alcoholic potash *p*-anisic acid and *p*-ethoxy-benzoic acid respectively.

(I)



$$\left.\begin{array}{r}CH_3OC_6H_4\\ C_2H_5OC_6H_4\\ C_2H_5OC_6H_4\end{array}\right\rangle C-CO-C_6H_4OCH_3$$

(II)



$$\left.\begin{array}{r}CH_3OC_6H_4\\ CH_3OC_6H_4\\ C_2H_5OC_6H_4\end{array}\right\rangle C-CO-C_6H_4OC_2H_5$$

In order to determine which of these two possible pinacolines has been actually obtained, the reduction product was hydrolysed by boiling with 20% alcoholic potash for twelve hours. After distilling off alcohol under diminished pressure, water was added to dissolve the potassium salt of organic acid. The neutral product which present as precipitates was extracted with benzene. The aqueous solution was acidified with sulphuric acid and was extracted with benzene. After removal of the solvent, the acid was treated with boiling water, in which *p*-anisic acid should be readily soluble while *p*-ethoxybenzoic acid only in trace. Actually the product was found dissolved in hot water completely. By repeated recrystallisations from hot water, fine colourless needles melting at 184°C. were obtained, which were identified as *p*-anisic acid by mixed melting point test, and by optical properties of the crystals. Thus the pinacoline was proved to be 4-methoxyphenyl-bis(4′-ethoxyphenyl)-4″-methoxybenzoyl-methane, corresponding to formula I.

(b) *Reduction by Absolute Alcohol under Direct Sunlight.* Methoxyethoxybenzophenone, dissolved in hot absolute alcohol, was sealed in a tube and exposed under direct sunlight. White crystals which fulfilled the tube disappeared in the course of several days and lightly yellowish-brown solution was obtained. The formation of acetaldehyde was easily detected by its peculiar smell and the sharp colour reaction toward Schiff's reagent. On distilling alcohol off under reduced pressure, greenish-gray soft mass was obtained, which was easily soluble in ordinary solvents except petroleum ether and ligroin. The crude product was dissolved in small amount of alcohol and the solution was kept below 0°C. In the course of few days crystals appeared, from which the mother liquor was decanted off. But as the crystals were still contaminated with sticky impurities, dissolution and cooling were repeated twice, and finally they were purified from ether. The product crystallises in granules, melting at 160°C., and dissolves in concentrated sulphuric acid with colouration of dark brown which changes to intense bluish-purple. No depression of melting point was observed when mixed with the pinacoline obtained by reducing the original ketone by zinc dust and glacial acetic acid. From the fraction readily soluble in alcohol no definite compound could be isolated.

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