

**On the Catalytic Action of Japanese Acid Earth. XI\*. The Isomerisation of Aldehydes to Ketones and the Explanation of the Migration of the Radicals from the Standpoint of the Electronic Theory.**

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**Introduction.** S. Daniloff<sup>(1)</sup> first observed that di- or trisubstituted acetaldehydes are partly transformed into the corresponding ketones, when warmed with acidic substances such as dilute sulphuric acid or a mixture of hydrochloric and acetic acids, or when treated with phosphorus pentachloride at ordinary temperature, while they are completely changed

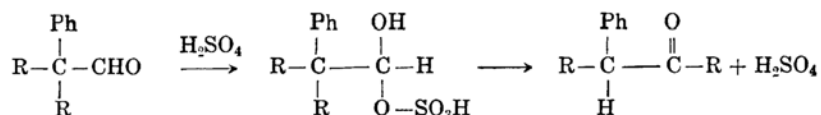
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\* X., this Bulletin, **10** (1935), 1

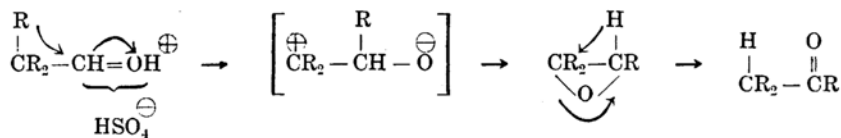
(1) *J. Russ. Phys. Chem. Soc.*, **49** (1917), 282; *ibid.*, **51** (1919), 97; *ibid.*, **57** (1925), 428; *Ber.*, **59** (1926), 377; *ibid.*, **60** (1927), 2390; S. Daniloff and E. Venus Danilova, *Ber.*, **59** (1926), 1032; *ibid.*, **60** (1927), 1050; *ibid.*, **62** (1929), 2653; *ibid.*, **63** (1930), 2269, 2765; E. Venus Danilova, *Ber.*, **61** (1928), 1954.

into ketones by the action of concentrated sulphuric acid at about  $-10^{\circ}\text{C}$ . The oximes of the aldehydes also yield ketones on heating with dilute sulphuric acid, but in this case the reaction product contains a certain quantity of the original aldehydes. Similar facts were observed by A. Orekhoff and M. Tiffeneau.<sup>(2)</sup> Later M. Tiffeneau<sup>(3)</sup> has studied extensively with his collaborators along this line, aiming to explain the relation between the "migratory tendency" and "capacity of affinity" of various organic radicals. They seem to hold the view that the migratory tendency as well as the capacity of affinity of organic radicals is a certain definite property of each radical and they concluded that a parallel relation does not always exist between these two properties. M. Migita<sup>(4)</sup> studied the pinacolinic rearrangement as a method of determining the relative electronegativities of organic radicals. He explained lucidly the facts observed by himself and others from the standpoint of the electronic theory of valency, which have previously been regarded apparently contradictory and not interpreted satisfactorily.

It appears, as J. W. Baker<sup>(5)</sup> suggested, that the rearrangement of the aldehydes mentioned above results from the actual interaction between the aldehydes and the strong acidic substances, giving rise to certain intermediate compounds, which are subsequently decomposed into the ketones isomeric to the original aldehydes. Thus in the presence of sulphuric acid the initial stage of the isomerisation may be the addition of a molecule of sulphuric acid to the aldehyde and the resulting sulphuric ester of the glycol may then undergo an ordinary pinacolinic rearrangement so as to give the ketones.



Another explanation was given by C. W. Shoppee<sup>(6)</sup> who suggested that sulphuric acid may function in the conversion of the carbonyl oxygen into the type of an oxonium salt, the attraction of positive charge so formed initiating the necessary electronic displacements resulting in the formation of an ethylene oxide, which then undergo a further pinacolinic change.



Different mode of combination may be possible, however, between aldehydes and the acidic reagents according to the nature of the latter.

(2) *Compt. rend.*, **182** (1926), 67.

(3) *Bull. soc. chim.*, **49** (1931), 1595-1860 (twenty-two papers).

(4) *This Bulletin*, **3** (1923), 308; *ibid.*, **4** (1929), 57, 225; *ibid.*, **7** (1932), 334, 341, 377, 382; *ibid.*, **8** (1933), 22, 27.

(5) Baker, "Tautomerism", (1934), 292.

(6) Thesis, London, 1929; (Baker, "Tautomerism", 1934, 292).

Consequently the intermediate compounds thus formed may have different intramolecular structures and show different chemical behaviours. It is clear that the subsequent decomposition of such an intermediate compound may take a different course giving rise sometimes to one and sometimes to other ketone, isomeric to each other, depending on the reagent as well as on the experimental conditions.

There is another type of reaction leading to the same isomerisation, i.e., isomerisation by thermal effect in the presence of catalysts. It was observed for the first time by Ramart-Lucas<sup>(7)</sup> and her collaborators. They distilled polysubstituted ethylene glycols, ethylene oxides and acetaldehydes over diatomaceous earth at different temperatures ranging from 200 to 600°C. under the reduced pressure of about 10 mm., and obtained various types of ketone, aldehyde, and hydrocarbon. The kinds and structures of these reaction products were found to depend chiefly upon the reaction temperature. They used the ultraviolet absorption spectra of these compounds for the study of the molecular rearrangement, and found that the "ascending branch" of the absorption curve of the more stable substance lies always nearer to the visible part than that of the less stable, when a rearrangement of a less stable substance into a more stable one takes place, preceded or followed by the elimination of a molecule of water, acid or salt. Thus the "ascending branch" of the absorption curve of glycol is placed farthest and that of the corresponding ketone nearest to the visible part, while that of aldehyde lies in an intermediate position; and hydrocarbon of the related structure, if produced, will exhibit its absorption curve with an "ascending branch" lying nearest to the visible part. Of the two isomeric ketones the one more stable at higher temperature always shows deeper absorption than the less stable. Thus it is a natural course, according to their opinion, that glycols are converted by thermal effect successively into aldehydes, ketones, and hydrocarbons. They further supposed that the study of the absorption spectra in the ultraviolet region would, therefore, enable them to predict which ketone will be produced from a certain aldehyde when there is a possibility of obtaining two isomeric ketones. No actual example of isomerisation of this type was, however, given by them so far as the author knows.

S. Daniloff<sup>(8)</sup> also observed the same type of isomerisation in the cases of substituted acetaldehydes, which were easily transformed into the isomeric ketones by thermal effect; thus by passing aldehydes over anhydrous aluminium sulphate heated at about 350°C. he obtained ketones isomeric to the aldehydes, and reasonably remarked<sup>(9)</sup> that it is natural that the less stable aldehydes may isomerise into the more stable ketones, that is to say, a substance with greater heat of combustion isomerises into that with the smaller.

In the present research a number of disubstituted acetaldehydes have been newly synthesised and subjected to isomerisation into the corresponding ketones in order to find which ketone of the two possible isomers

(7) *Compt. rend.*, **186** (1928), 1301; *ibid.*, **186** (1928), 1626, 1848; *ibid.*, **188** (1929), 638, 1301; *Bull. soc. chim.*, **45** (1929), 478, 718; *ibid.*, **49** (1931), 1860.

(8) *J. Russ. Phys. Chem. Soc.*, **62** (1929), 723.

(9) *Ber.*, **60** (1927), 1056.

will thereby be produced, and the results have been explained from the standpoint of the electronic theory of organic compounds.

The isomerisation was carried out in the presence of Japanese acid earth. Its catalytic action at high temperatures has already been investigated by Dr. H. Inoue and the present author<sup>(10)</sup> on various organic compounds, and has been shown to be far stronger than those of alumina and silica, the chief components of the acid earth. It was also confirmed by the present author\* that the existence of water in addition to the two components is indispensable for the characteristic catalytic action of the earth, and was suggested that these three components must be suitably oriented on the surface of the earth in order to form the catalytically "active centres." When a molecule of an organic compound is adsorbed on the "active centre" thus formed, it must also be oriented suitably on this centre in order to get activated. The interatomic bonds of a molecule thus adsorbed on an active centre, will consequently be weakened and the atoms will rearrange themselves within the molecule so as to gain a more stable structure, leading to the observed transformation.

**Experimental Procedure.** *Conditions of the Experiment and Manipulation.* The middle part converging 33 cm. of a Jena glass tube with an inner diameter of 1.5 cm. was filled with granules of Japanese acid earth with diameters from 1.5 to 3.0 mm.. The tube was heated at 300°C. and maintained at that temperature during the experiment in a horizontal electric furnace slightly inclined, and then the aldehyde was passed into it drop by drop with a rate from 3 to 4 g. per hour. A slow flow of carbon dioxide through the tube served to prevent the oxidation of the aldehyde by atmospheric oxygen and to carry away the reaction products. A receiver connected with the end of the tube was cooled with ice water to collect the reaction products. When all of the aldehyde was passed in and no more reaction product (i) was observed to come out of the tube, the receiver was changed and the whole reaction system was evacuated, the temperature being maintained at 300°C. meanwhile, and some more product (ii) was obtained. The receiver was again changed and the temperature was raised to 350°C. under the reduced pressure and a further portion of the product (iii) was obtained. The product (i) usually consisted of an easily flowing colourless liquid (mainly hydrocarbon) mixed with water drops, while the products (ii) and (iii) were for the most part colourless or yellowish fragrant viscous oils which solidified on cooling to crystalline masses. In some cases the temperature of the reaction tube was finally raised to 450°C. under the reduced pressure and a reddish brown viscous oil mixed with a small quantity of crystals was obtained. Each product was separately subjected to suitable treatments to isolate and identify the individual substances contained in it, and to estimate their relative quantities.

*Confirmation and Analysis of the Reaction Products.* In every case no trace of the aldehyde unchanged was found to exist in the reaction

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(10) H. Inoue, this Bulletin, **1** (1926), 157, 177, 197, 219; H. Inoue and K. Ishimura, *ibid.*, **9** (1934), 423, 431; K. Ishimura, *ibid.*, **9** (1934), 493, 522; *ibid.*, **10** (1935), 1.

\* *Loc. cit.*

products. The ketones produced by the isomerisation were mostly obtained as solid crystalline mass. Their constitutions were confirmed by the Beckmann rearrangement of their oximes on one hand and by synthesis on the other, as described below.

When two isomeric ketones were formed simultaneously by the isomerisation of one aldehyde, the exact analysis of the experimental results became sometimes very difficult, for the isolation of both the ketones followed by the estimation of their relative quantities was not an easy work. A simple thermal analysis carried out beforehand proved very useful in such cases. Equilibrium diagrams of the systems of phenyl-*p*-methylbenzyl ketone and *p*-tolylbenzyl ketone and of *p*-chlorophenyl-*p*-methylbenzyl ketone and *p*-tolyl-*p*-chlorobenzyl ketone were drawn, which much helped to determine the compositions of the reaction mixtures. Rheinboldt's method<sup>(11)</sup> was modified for this purpose; definite quantities of the two compounds synthesised and purified by appropriate methods were intimately mixed, molten, crushed and pulverised after cooling and put in small capillaries of about 40 mm. in length and from 1 to 2 mm. in diameter. The determination of the thawing as well as melting points was carried out in the same manner as the molecular weight determination by Rast's method. Reliable results were obtained as well without stirring the content of the capillary with a slender glass rod inserted into it, as proposed by Rheinboldt. Thus a very small quantity of materials was enough to complete one series of experiment and the time required for the determination was considerably shortened.

As shown in Fig. 1 and 2 it has been found by the author that a eutectic point exists in the system of phenyl-*p*-methylbenzyl ketone and

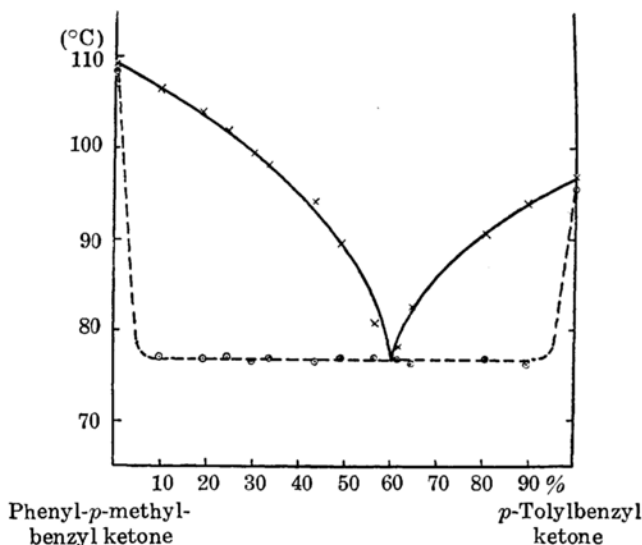


Fig. 1. Equilibrium diagram of the system: phenyl *p*-methylbenzyl ketone and *p*-tolylbenzyl ketone.

(11) *J. prakt. Chem.*, [2] **111** (1925), 242; *ibid.*, **112** (1926), 187; *ibid.*, **113** (1926), 199. Pfeiffer, "Organische Molekülverbindungen", (1927) 66-85.

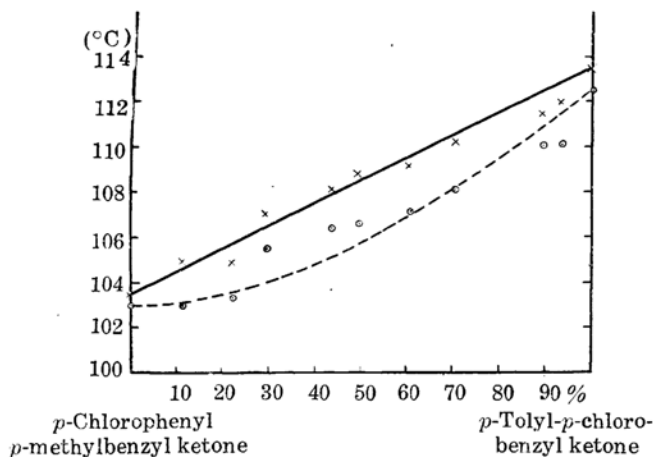
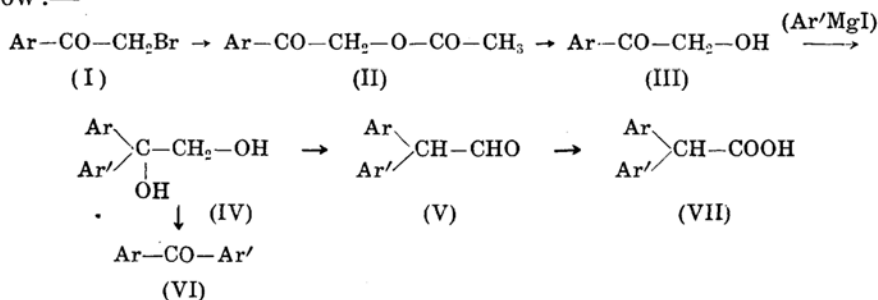


Fig. 2. Equilibrium diagram of the system:  $p$ -chlorophenyl- $p$ -methylbenzyl ketone and  $p$ -tolyl- $p$ -chlorobenzyl ketone.

$p$ -tolylbenzyl ketone, while in that of  $p$ -chlorophenyl- $p$ -methylbenzyl ketone and  $p$ -tolyl- $p$ -chlorobenzyl ketone a diagram characteristic to solid solution has been obtained.

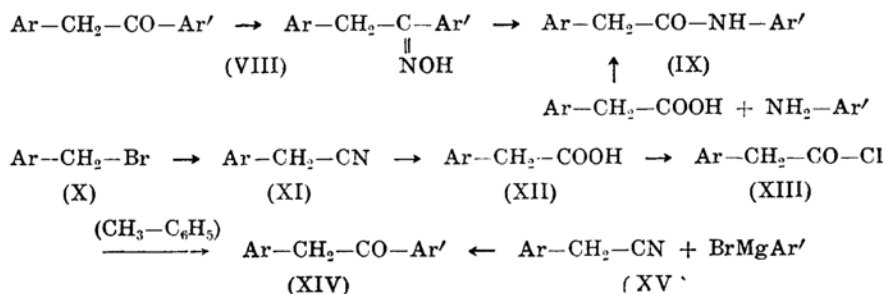
**Materials and Products.** The aldehydes employed in the present experiment were synthesised according to the general scheme shown below:—



$\omega$ -Bromacetophenone and  $\omega$ -bromo- $p$ -methylacetophenone (I) were interacted with potassium acetate in alcoholic solution giving the corresponding acetates (II), which on hydrolysis by boiling with barium carbonate were changed respectively to benzoyl carbinol and  $p$ -methylbenzoyl carbinol (III). By Grignard reaction with aryl magnesium iodide they gave  $\alpha, \alpha'$ -diaryethylene glycols (IV) which suffered intramolecular rearrangement accompanied by the splitting of a molecule of water, when heated at about  $115^\circ\text{C}$ . with crystalline oxalic acid mixed with a small quantity of water for three hours, or when heated at about  $180^\circ\text{C}$ . for several hours, with a mixture of water and a few drops of concentrated sulphuric acid in a sealed tube, resulting in the formation of the required aldehydes (V).

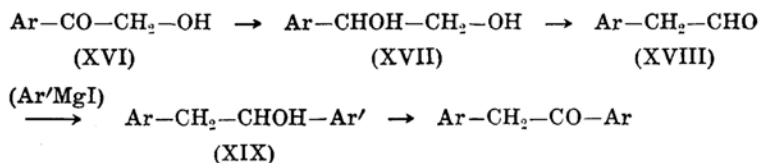
The constitutions of the glycols and the aldehydes were confirmed by oxidising them to diaryl ketones (VI) and diarylacetic acids (VII) respectively.

The ketones produced by the isomerisation of the aldehydes were identified by the Beckmann rearrangement of their oximes on one hand and by synthesis on the other, as schematically shown below:—



The oxime (VIII) of the ketone was dissolved in dry ether and phosphorus pentachloride was added little by little, and the reaction product was poured into ice water, and the solid mass separated was purified by recrystallisation from alcohol, which was identified with the product (IX) obtained by the interaction between arylacetic acid and arylamine.

Tolyl and xylyl bromides (X) were converted successively into cyanides (XI), carboxylic acids (XII) and acid chlorides (XIII) which were condensed with toluene in the presence of anhydrous aluminium chloride, thus the required ketone (XIV) were synthesised. The ketones were also obtained from arylacetonitriles (XV) by the action of aryl magnesium iodide. A third method of obtaining the same ketone is the oxidation of diarylcarbinol (XIX) produced from arylacetaldehyde (XVIII) by the Grignard reaction, which was in its turn produced by heating aryloethylene glycol (XVII) at about 180°C for four hours in a sealed tube with water and a few drops of concentrated hydrochloric acid.



The aryloethylene glycol (XVII) was obtained by the catalytic hydrogenation of aroylcarbinol (XVI) under the ordinary pressure with colloidal platinum as catalyst.

*Purification of m-Tolyl-p-Tolyl Acetaldehyde.* It has been observed by the present author that a large quantity of *m*-tolyl-*p*-tolyl ketone was sometimes produced when the purification of *m*-tolyl-*p*-tolyl acetaldehyde was carried out through its addition compound with sodium bisulphite or when it was oxidised to the corresponding acid with moist silver oxide. Similar facts have been also observed in the case of *p*-tolyl-*p*-chlorophenyl acetaldehyde. The mechanism of the reaction is for the time left open. F. W. Semmler<sup>(12)</sup> observed that enolacetates of aldehydes of the types

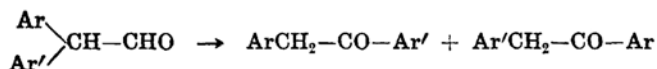
(12) *Ber.*, **42** (1909), 588, 962; *ibid.*, **43** (1910), 1724, 1890.

$RCH_2CHO$  and  $RRCHCHO$  are changed to the acid  $RCO_2H$  and the ketone  $RCOR$  respectively when oxidised with ozone or permanganate.

*Separation of o- and p-Isomers of Xylyl Derivatives.* As the starting materials for the synthesis of ketones of the type  $ArCH_2COAr'$  the three isomers of xylene were used as mentioned above (p. 202), each of which usually contains small quantities of its isomers as impurities. According to P. Hill and W. F. Short<sup>(13)</sup> the pairs of *o*- and *p*-isomers of xylyl chlorides, alcohols, acetates as well as cyanides boil at the same temperature and cannot be separated by fractional distillation, whilst *o*- and *p*-tolylacetic acids form a continuous series of solid solutions. On the contrary, the present author has found that the corresponding acid amides can be easily separated from each other by fractional crystallisation from boiling water and the purification of the related substances was always carried out quite well at this stage of preparation.

*Autoxidation of Ketones of the Type  $ArCH_2COAr'$ .* The ketones of the type  $ArCH_2COAr'$  such as *o*-tolyl-*p*-methylbenzyl, *m*-tolyl-*p*-methylbenzyl, *p*-chlorophenyl-*p*-methylbenzyl and *p*-tolyl-*p*-chlorobenzyl ketones have been found to be converted largely into the mixtures of the corresponding arylacetic acids, on standing in the presence of light and air for several months. Similar facts were observed by E. C. Fortey<sup>(14)</sup> and by S. S. Jenkins.<sup>(15)</sup>

**Results of Isomerisation Experiments.** Four diarylacetaldehydes were employed in the present work. They were subjected to the intramolecular rearrangement in the presence of Japanese acid earth under the conditions stated above and all gave the corresponding ketones.



(1) Phenyl-*p*-tolyl acetaldehyde has given phenyl-*p*-methylbenzyl ketone exclusively, in other words, only the phenyl group has migrated.

(2) *m*-Tolyl-*p*-tolyl acetaldehyde has given *m*-tolyl-*p*-methylbenzyl ketone exclusively, that is only the *m*-tolyl group has migrated.

(3) *o*-Tolyl-*p*-tolyl acetaldehyde has given a mixture of *o*-tolyl *p*-methylbenzyl and *p*-tolyl-*o*-methylbenzyl ketones. The ratio of the yield in the former ketone to that in the latter was found to be about 4:1, showing that in this case the *o*-tolyl group has a migratory tendency about four times as large as that of the *p*-tolyl group.

(4) *p*-Tolyl-*p*-chlorophenyl acetaldehyde has been changed mainly to *p*-chlorophenyl-*p*-methylbenzyl ketone accompanied by a small quantity (about one tenth of the foregoing ketone) of *p*-tolyl *p*-chlorobenzyl ketone, showing that the *p*-chlorophenyl group has a very large migratory tendency in comparison with the *p*-tolyl group in this case.

Thus these results clearly show that the order of the migratory tendency of the aryl groups is as follows:—

Phenyl, *m*-tolyl > *p*-chlorophenyl > *o*-tolyl > *p*-tolyl.

(13) *J. Chem. Soc.*, **1935**, 1126.

(14) *J. Chem. Soc.*, **75** (1899), 871.

(15) *J. Am. Chem. Soc.*, **57** (1935), 2733.



**Discussion of the Results.** *Nature of the Catalyst in the Isomerisation.* Japanese acid earth employed as catalyst in the present experiment is a kind of clay abundantly produced in many districts in Japan. It resembles Fuller's earth and Florida earth in many respects and is essentially a certain type of hydrated aluminium silicate mixed with colloidal silica<sup>(16)</sup> and small amounts of many other metallic oxides. Its average composition is as follows:—

SiO<sub>2</sub>, 60–72; Al<sub>2</sub>O<sub>3</sub>, 13–20; Fe<sub>2</sub>O<sub>3</sub>, 2–4; CaO, 0.5–2; MgO, 1–5; K<sub>2</sub>O+Na<sub>2</sub>O, 0.5–1.8; ignition loss, 7–15%.

The earth is designated "acid" because it turns a blue litmus paper red when placed on the paper and moistened with a few drops of water. But the colour change is restricted only to the neighbourhood of that part of the paper which is directly in contact with the earth. This phenomenon was explained as due to its characteristic selective adsorptive power for hydroxyl ion.<sup>(17)</sup> The earth also manifests various oxydase-like colour reactions, e.g. the reactions for indophenol, potassium iodide, leuco-base of malachite green and benzdine.<sup>(18)</sup> When suspended in the water solution of pyrogallol the earth oxidizes it gradually.<sup>(19)</sup> Cane sugar and starch are hydrolysed into invert sugar<sup>(20)</sup> and maltose<sup>(21)</sup> respectively, when their water solutions are shaken with the earth. All these reactions also, the author believes, may be ascribed to the hydrogen ion generated as the result of the selective adsorption mentioned above.

In dry state, especially when dehydrated at 200–300°C., the earth adsorbes ammonia, vapours of water, alcohols, ketones, ethers, etc.. The adsorption of these vapours takes place very strongly, sometimes with the evolution of considerable quantity of heat, the adsorbates being retained tenaciously on it.<sup>(22)</sup> At high temperature, water or ammonia is eliminated from the organic adsorbates when the organic molecules contain hydroxyl or amino group, and the dehydration or deamination is accompanied very often by intramolecular rearrangements. Thus cyclohexanol and their methyl derivatives have been found to produce cyclohexene and its methyl derivatives together with methylcyclopentane and dimethylcyclopentanes respectively,<sup>(23)</sup> when passed on the earth heated at 300–350°C. Cyclohexylamine and its methyl derivatives have similarly given cyclopentane series,<sup>(24)</sup> showing that the six-membered carbon ring was converted into the five-membered one.

The elimination of water or ammonia may be induced by the initial attraction of hydroxyl or amino group towards the earth, and these negative groups tend to be ionized and will be splitted as anions. If the remain-

(16) K. Yamamoto, *J. Soc. Chem. Ind. Japan*, **34** (1931), 244B; *ibid.*, **36** (1933), 38B, 460B.

(17) Y. Tanaka and T. Kuwata, *J. Soc. Chem. Ind. Japan*, **32** (1929), 290B; Y. Tanaka, T. Kuwata and S. Furuta, *ibid.*, **35** (1932), 224B.

(18) K. Kobayashi and K. Yamamoto, *ibid.*, **26** (1923), 23B.

(19) H. Kaneko, *J. Chem. Soc. Japan*, **45** (1924), 189.

(20) T. Okuno, *J. Soc. Chem. Ind. Japan*, **28** (1925), 54B.

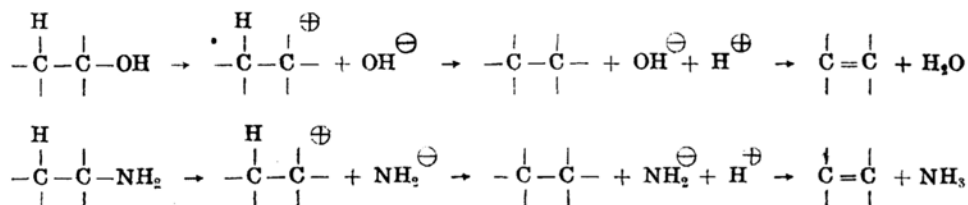
(21) B. Kato, *J. Zymurgy* (in Japanese), **2** (1924), 1023.

(22) K. Ishimura, *this Bulletin*, **10** (1935), 2.

(23) H. Inoue, *loc. cit.*

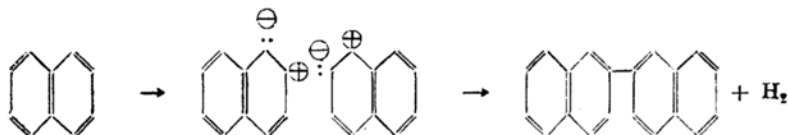
(24) K. Ishimura, *loc. cit.*

ing positively charged fragment has a hydrogen atom attached to it, it can be stabilised by the loss of a proton which then unites with the splitted anion to form water or ammonia molecule, as schematically shown below:—



When the removal of a proton occurs at  $\alpha$ -carbon atom with respect to hydroxyl or amino group as shown above, cyclohexane series will be produced. But if it occur at  $\beta$ -carbon atom the molecular rearrangement will take place resulting in the formation of cyclopentane series.

H. Inoue and the present author<sup>(25)</sup> have formerly found that when a mixture of naphthalene and some dry powdered Japanese acid earth is heated at about 300°C. in a sealed tube, a marked amount of a resinous matter is produced, which is mainly composed of  $\beta$ ,  $\beta'$ -dinaphthyl. The formation of  $\beta$ ,  $\beta'$ -dinaphthyl from naphthalene by the catalytic action of the earth may be explained similarly: by the electron-attracting property of the earth the molecule of naphthalene is polarized<sup>(26)</sup> and an unshared electron pair is placed on that carbon atom which is attracted by the earth, leaving positive charge on some other carbon atom. When another molecule of naphthalene comes into the force field of the molecule thus polarized, it will, according to the author's opinion, in turn be polarized and in consequence the combination of the proton and the hydrogen anion will take place to produce a hydrogen molecule, accompanied by the formation of the dinaphthyl. There are equal chance for  $\alpha$ - and  $\beta$ -positions thus to be polarized, but the effect of steric hindrance will lead to the formation of  $\beta$ ,  $\beta'$ -dinaphthyl exclusively. The process may be given as follows:—



It is therefore very reasonable to admit that the essential function of Japanese acid earth as catalyst is that of attracting unshared electron pairs in the molecules of adsorbates to form co-ordinate links with certain positive centres situated on the surface of the earth, probably with silicon or aluminium atom or both. At least the fundamental action of the earth must consist in bringing a positive potential into the molecules adsorbed on it.

(25) This Bulletin, 9 (1934), 432.

(26) L. Pauling, "The Nature of the Chemical Bond," (1940), 152.

*Mechanism of Isomerization.* When a molecule of disubstituted acetaldehydes  $RR'CHCHO$  approaches to the surface of the earth, an unshared electron pair of the carbonyl oxygen is attracted by the earth.

Now in normal state the resonance between the structures



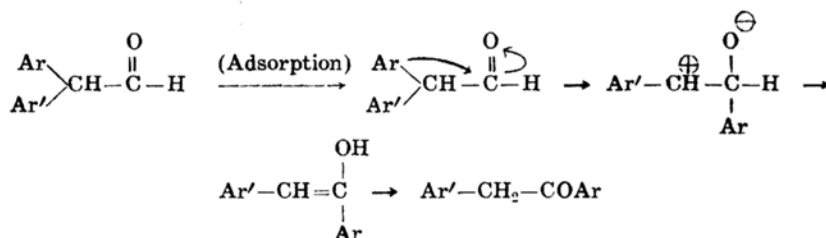
(with a very small contribution from  $\begin{array}{c} \text{R} \\ \diagup \\ \text{CH} - \overset{\oplus\oplus}{\text{C}} \overset{\ominus\ominus}{\text{O}} \\ | \\ \text{H} \end{array}$ ) takes place in the

aldehyde molecule, and evidences are given that the amount of the ionic character (single bond character) of the carbonyl carbon is about 50 percent, by the measurement of electric dipole moments of various ketones and aldehydes as well as by the electronegativity difference for carbon-oxygen bond.<sup>(27)</sup> But in the adsorbed molecule of an aldehyde the electronic distribution within the molecule is disturbed, and consequently an

electronic displacement of electrons in the carbonyl group  $\overset{\curvearrowright}{\text{C}}=\text{O}$  will be promoted, so that the single bond character of the carbon-oxygen link is greatly enhanced, leaving the carbon atom with an open sextet of electrons, and the resonance is destroyed.

In this activated state the depletion of the octet round the carbonyl carbon atom necessitates the migration of an anion towards it from the adjacent  $\alpha$ -carbon atom. The demand for negative charge of the  $\alpha$ -carbon atom, from which the anion is detached, will then cause the splitting of a proton from the carbonyl carbon followed by the flow of electron pairs from the latter carbon atom towards the former. If it is a hydrogen atom that is first removed as anion from the  $\alpha$ -carbon atom, there would take place only the wandering of two hydrogen atoms exchanging their positions of attachment, and thus no actual rearrangement would occur. But if one of the aryl groups migrates with its valency electrons, the proton splitted from the carbonyl carbon will unite with the oxygen, so that a ketone will be produced in the enolic form.

The rearrangement visualized as above will occur according to the following scheme:—



In the systems otherwise identical, as in the present case, it is to be expected that the tendency to migration of different anions would follow their order of anionic stability. As it is generally accepted, the hydrogen

(27) L. Pauling, *loc. cit.*, 152.

anion is very unstable, and one of the aryl groups, therefore, will be separated. Which of the two aryl groups, then, will be separated first is, determined by the magnitude of their capacity for electron-attraction; the more electron-attracting group will more easily be separated. When the capacities for electron-attraction of the two groups are not greatly different, there is the possibility of the simultaneous separation of the two groups, giving rise to a mixture of two isomeric ketones, their relative yields depending upon the relative capacity for electron-attraction of the migrating groups.

If the proton and the anion thus successively separated pass outside the force field of the rearranging molecule, they may combine directly to give rise to the formation of hydrocarbons. Thus benzene and toluene have been actually confirmed to exist in the reaction products of the present experiment in considerable quantities.

According to J. W. Baker's<sup>(28)</sup> opinion the initial stage of the rearrangement of the aldehyde by the action of sulphuric acid is possibly the addition of a molecule of the acid to the aldehyde and the sulphuric acid ester of the glycol so formed may then undergo an ordinary pinacolinic electron displacement with hydrogen migration to give the ketone. C. W. Shoppee<sup>(28)</sup> has explained the conversion, as above stated, by assuming the intermediate formation of an ethylene oxide. But in the case of the present work the mechanism involving the actual formation of either glycol or ethylene oxide as intermediates seems untenable. R. Lagrave<sup>(29)</sup> distilled under the reduced pressure a series of ethylene

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oxides of the general formula  $(\text{Ph})_2\text{C}=\text{C}-\text{CHR}$  and obtained as the major product the ketone  $(\text{Ph})_2\text{CH}-\text{CO}-\text{R}$  but found that the considerable quantity of the aldehyde  $(\text{Ph})_2\text{CR}-\text{CHO}$  was also produced, where Ph and R represent phenyl and alkyl groups respectively. Therefore, if the transformation of an aldehyde into an isomeric ketone be effected through the intermediate formation of an ethylene oxide, there should exist an equilibrium between the aldehyde and the ethylene oxide under such conditions. No trace of either aldehyde or ethylene oxide, however, was found in the reaction product.

The experimental results obtained by Ramart-Lucas and Jean-Pierre Guerlain<sup>(30)</sup> are in good accordance with those of the present experiment. They passed aldehyde of the type  $\text{ArRCHCHO}$  over diatomaceous earth heated at 500–600°C. as above stated and obtained ketones of the type  $\text{ArCH}_2\text{COR}$  as the main product together with some quantity of the unchanged original aldehydes. It is natural in the light of the consideration above given that the alkyl group R migrates in preference to the aryl group Ar, since it has a smaller capacity for electron-release. The reaction temperature was, however, by far higher than in the case of the present experiment and yet there remained a portion of aldehyde unchanged. These facts may be explained by the weaker activity of the catalyst, in other words, by the smaller capacity for electron-attraction of diatomace-

(28) "Tautomerism", (1934), 292.

(29) *Ann. chim.*, [X], 8 (1927), 363.

(30) *Bull. soc. chim.*, 45 (1929), 478, 718; *ibid.*, 49 (1931), 1860.

ous earth in comparison with Japanese acid earth. The far weaker catalytic activity of the former than that of the latter has been shown by the present author<sup>(31)</sup> by comparing the activity for producing  $\beta$ ,  $\beta'$ -dinaphthyl from naphthalene.

*Comparison of the Capacity for Electron-release of the o- and p-Tolyl Groups.* As above stated, in the author's experiment, when diarylacet-aldehydes rearrange into the corresponding ketones, phenyl-, o-tolyl-, m-tolyl and p-chlorophenyl radicals migrate in preference to the p-tolyl radical, showing that the last mentioned possesses the greatest capacity for electron-release.

Since the methyl group tends to produce an effect of electron-release relative to hydrogen, when it is attached to the benzene nucleus, it loses electrons to the ring; they go mainly to the ortho and para carbon atoms. This capacity of the methyl group to repel electrons has been regarded as due to its inductive effect only and the tautomeric effect of the methyl group is inconceivable from the standpoint of ordinary organic chemical theory. J. W. Baker and W. S. Nathan<sup>(32)</sup> suggested, however, that the methyl group, when directly attached to a conjugated system, is capable of permitting electron-release by a mechanism which is assumed to function in addition to the inductive effect and in essentials is of the type of

tautomeric effect  $\text{H}-\text{CH}_2-\text{C}=\text{C}-\text{C}-$  much as if the electrons were unshared as in chlorine. The inductive effect of the methyl group will thus be greatly reinforced. By applying the new idea the English authors gave a satisfactory explanation to various points till then obscure in organic chemistry and found furthermore, together with C. W. Shoppee,<sup>(33)</sup> that the new postulated mechanism is of not an electromeric but of a mesomeric (permanent) type. The definite demonstration of the reality of the tautomeric electron displacements of the electrons of nonionizing CH-groups was then made by the study of E. D. Hughes, C. K. Ingold, N. A. Taher and L. C. Bateman.<sup>(34)</sup> Recently Y. Tsuzuki, T. Uemura and N. Hirasawa<sup>(35)</sup> found that the absorption bands of o- and p-nitrosotoluenes are shifted to a longer wave length relative to that of nitrosobenzene. They ascribed the fact to the tautomeric but not inductive effect of the methyl group situated in the ortho and para positions with regard to nitroso group. They showed moreover that the methyl group in the para position exerts a much stronger effect than those in the ortho and meta positions. The results of the present work lead also to the same conclusion. Thus the o-tolyl group migrated to a larger degree than the p-tolyl group as already stated (p. 203). These results apparently contradict with the facts that in the aromatic substitution the methyl group appears to be more nearly ortho-orienting than any other.<sup>(36)</sup> It is tentatively suggested here that the smaller effect of the methyl in the ortho position or the greater ease with which the o-tolyl group separates as anion may be

(31) This Bulletin, **9** (1934), 498.

(32) *J. Chem. Soc.*, **1935**, 1844.

(33) *Ibid.*, **1935**, 1847.

(34) *J. Chem. Soc.*, **1940**, 949, and subsequent papers.

(35) *J. Chem., Soc., Japan*, **61** (1940), 1063.

(36) J. B. Rease, *Chem. Reviews*, **14** (1934), 77.

ascribed to the formation of hydrogen bond between hydrogen in the methyl and carbonyl (or nitroso) oxygen: it is very probable that an alkyl group can form a hydrogen bond, provided that an electron-donating atom is suitably placed with respect to it.

*Comparison of the *p*-Tolyl and *p*-Chlorophenyl Radicals.* A greater resistance of the *p*-tolyl (and *o*-tolyl) group to ionisation in comparison with the *p*-chlorophenyl group, indicated by its smaller tendency to migration, can be explained by taking into consideration the inductive effect (+I) in the methyl group as above visualised on one hand and the well known inductive effect (-I) in chlorine atom superimposed on the electromeric effect of the opposite sign (+T) on the other. The action of the electromeric effect (+T) in chlorine atom is diminished by the inductive effect of its own, if not totally suppressed, by the flow of electrons towards it from  $\alpha$ -carbon atom.

Quite recently Y. Tsuzuki, T. Uemura and N. Hirasawa<sup>(37)</sup> reached to the conclusion that the *p*-tolyl group has a greater capacity for electron-release than the *p*-chlorophenyl group by studying the effect of para-substituents to shift the absorption band of nitrosobenzene to a longer wave length. Their results accord well with that of the present work.

*Comparison of the *m*-Tolyl and Phenyl Groups.* The methyl group in the meta position exhibits a simple inductive effect but not a mesomeric effect as in the cases of para and ortho derivatives. The *m*-tolyl group shows therefore a much smaller tendency to migration, as clearly shown by the non-existence of *p*-methylbenzyl-*m*-tolyl ketone in the reaction product.

The phenyl group is capable of drawing an electric charge of either sign ( $\pm$ ), as generally admitted, by an electromeric electron displacements of either sign ( $\pm T$ ), when promoted by the requirement of the system. In the present case it may easily be ionised by absorbing electrons which will flow from the adjacent *p*-tolyl group. Thus the greater separability and the subsequent migration of the phenyl group may be expected in preference to the *p*-tolyl group, which actually took place.

Though the actual comparison of the relative mobility of the phenyl and *m*-tolyl groups has not been made, it is very probable that the phenyl group would be separated to a greater degree than the *m*-tolyl group owing to the inductive effect of an electron-release of the methyl group on one hand and to the inherent dual electronic character of the phenyl on the other. (*To be continued*).

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(37) *Ber.*, **74** (1941), 616.