

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 (Continued and concluded).

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α-o-Tolyl α-p-tolyl ethylene glycol. *p*-Methylbenzoyl carbinol (9.5 g) was added to the Grignard reagent (44 g. *o*-iodotoluene and 4.8 g. magnesium). After all of the carbinol was added the reaction mixture was boiled for 3 hours. It was cooled and treated with acetic acid (15 g. glacial acetic acid in 300 c.c. ice water). The upper ethereal solution was washed with dilute caustic soda, saturated solution of sodium chloride, and sodium bisulphite and again with brine. The ether was removed and the residue was subjected to the steam distillation for 5 hours. The contents of the flask were left to stand overnight. The main part (14.5 g.) of the required glycol settled down to the bottom forming yellowish solid mass, while a small portion (0.9 g.) of it was found to be suspending in water forming colourless needles, which crystallised from dilute alcohol in colourless needles, m.p. 115–116°C. (Found: C, 78.5; H, 7.7. $C_{16}H_{18}O_2$ requires C, 78.3; H, 7.4%).

The benzoyl derivative was obtained by Schotten-Baumann's method. It crystallised from 95% alcohol in colourless columns or needles, m.p. 164–165°C. (to a yellow melt). It has one molecule of water of crystallisation alike benzoyl *m*-tolyl *p*-tolyl ethylene glycol. (Found: C, 76.1; H, 6.0%; Mol. wt., (Rast), 325. $C_{23}H_{22}O_3 \cdot H_2O$ requires C, 75.8; H, 6.6%; Mol. wt., 364).

Oxidation of α-o-tolyl α-p-tolyl ethylene glycol. The glycol (0.83 g.) was added by portions to chromic oxide (1.2 g.) dissolved in 80% acetic acid (50 c.c.) and heated to boiling for a short time and left to stand overnight. It was neutralised with dilute caustic soda, extracted with ether, the ethereal extract washed with a solution of sodium chloride, dried over calcium chloride, the ether distilled off leaving an oil (0.55 g.), the crude *o*-tolyl *p*-tolyl ketone. The oxime produced from the ketone crystallised from dilute alcohol in colourless needles, m.p. 120°C. W. Scharwin and Schorygin⁽⁶⁸⁾ described the ketone as an oil boiling at 316–318°C./760 mm., characterised by an oxime melting at 122°C. The oxime was converted to *o*-tolyl *p*-toluidide through the Beckmann rearrangement, m.p. 144°C. (Found: N, 6.6. $C_{15}H_{15}ON$ requires N, 6.2%), which has also been given by the above-mentioned Russian authors.

α-Tolyl p-tolyl actaldehyde. A mixture of *α-o*-tolyl *α-p*-tolyl ethylene glycol (30 g.), crystalline oxalic acid (75 g.) and water (30 c.c.) was gently boiled for 3 hours, carbon dioxide being meanwhile passed into

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the reaction vessel in order to prevent the oxidation of the product with atmospheric oxygen. The upper layer of the contents of the vessel was extracted with ether, the ethereal extract washed with dilute caustic soda and with water, dried over anhydrous sodium sulphate and the ether was removed by distillation. The residue was distilled in the

reduced pressure of 9 mm. giving the fractions shown in Table 2.

Table 2.

Fractions	B.p. (°C.)	Yield (g.)
(1)	140-165	1.1
(2)	165-175	3.0
(3)	175-180	3.0
(4)	180-182	5.4
(5)	182-205	3.5
(6)	Residue	—

The fraction (1) consists chiefly of *p*-methylbenzoyl carbinol still remaining. The fraction (4) is the required aldehyde, d_4^{20} , 1.0669; n_D^{20} , 1.5812; M.R., found, 69.96; calc. (Eisenlohr), 68.90. (Found: C, 85.4; H, 7.5. $C_{10}H_{10}O$ requires C, 85.7; H, 7.1 %).

The aldehyde unites with sodium bisulphite very difficultly obviously owing to the steric hindrance of the methyl group attached to the carbon atom next to the carbonyl. A small quantity of *o*-tolyl *p*-tolyl ketone, which is still more difficult than the foregoing ketone to produce the addition compound with bisulphite, was found to be produced thereby. Its existence was confirmed by the production of *o*-toluyl *p*-toluidide, m.p. 143-144°C., (Found: N, 6.5. $C_{15}H_{15}ON$ requires N, 6.2%), from the oxime through the Beckmann rearrangement. The melting point did not depress by mixing it with the condensation product of *o*-toluic acid and *p*-toluidine.

o-Tolyl *p*-tolyl acetaldehyde forms a faintly yellow, viscous oil, and turns blue when brought to contact with Fuchsin-bisulphite solution. The semicarbazone crystallised from dilute alcohol in thick prisms, m.p. 154-155°C. (to a yellow melt). (Found: N, 15.2. $C_{17}H_{19}ON_3$ requires N, 14.9%).

o-Tolyl *p*-tolyl acetic acid. Potassium hydroxide (5 g. dissolved in 50 c.c. water) was added by portions (5 c.c. at a time every ten minutes) to the mixture of *o*-tolyl *p*-tolyl acetaldehyde (3 g. dissolved in 60 c.c. alcohol) and silver nitrate (7 g. dissolved in 7 c.c. water), and the mixture was shaken vigorously meanwhile. It was filtered, the filtrate saturated with carbon dioxide, concentrated on the water bath. The remaining aldehyde was thereby thrown down as oil drops, which were separated on filter paper. The filtrate was neutralised with dilute sulphuric acid. An oily substance separated, and solidified on cooling and crystallised from hot water in glittering plates (0.8 g.), m.p. 115-116°C. (Found: C, 80.2; H, 7.0%; Equiv. wt. (by titration with 1/20 N alkali solution), 239.8. $C_{16}H_{16}O_2$ requires C, 80.0; H, 6.7%; Equiv. wt., 240.1).

o-Tolyl *p*-methylbenzyl ketone. Attempts to prepare the above ketone by the condensation of ω -brom-*o*-methylacetophenone with toluene in the presence of anhydrous aluminium chloride failed, while the oxidation of *o*-tolyl *p*-methylbenzyl carbinol resulted in the formation of the impure ketone difficult to be purified. The pure ketone was obtained only by the isomerization of *o*-tolyl *p*-tolyl acetaldehyde. It melts at 26°C.

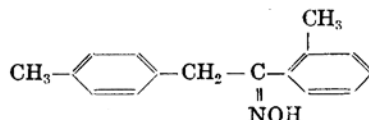
The preparation of the ketone from *o*-tolyl *p*-methylbenzyl carbinol was carried out in the following way. *p*-Tolyl acetaldehyde (2 g. dissolved in 2 c.c. ether) was added to the Grignard reagent (3.26 g. of *o*-tolyl iodide and 0.36 g. of magnesium), the reaction mixture was boiled for 2 hours and left to stand overnight. A small quantity of ice water was added to the product, followed by 36% hydrochloric acid (1.2 c.c.). It was then treated as usual and a yellow thick oil (1.3 g.) was obtained, which showed no tendency to solidify when cooled. The raw *o*-tolyl *p*-methylbenzyl carbinol (0.80 g.) thus obtained was dissolved in 80% acetic acid (30 c.c.) and chromic oxide (0.15 g.) was added to the solution little by little. The solution was boiled for 30 minutes, cooled and poured into ice water (400 c.c.), the water solution extracted with ether, the ethereal extract was washed with aqueous sodium hydroxide and with a solution of sodium chloride, dried over calcium chloride and the ether removed. A semi-solid yellow mass (0.37 g.) with aromatic odour was obtained, which did not solidify when cooled at -15°C . for 12 hours. Attempts to obtain the oxime from the ketone considered to have thus been produced resulted in the formation of viscous oil which again did not solidify when cooled at -5°C . It was dissolved in ether and treated with phosphorus pentachloride and the well defined crystals of [*p*-tolyl acetyl]-*o*-toluidide (0.05 g.), m.p. 163°C . (uncorr.), was finally obtained showing that the required ketone has actually been synthesised. The melting point was not depressed by mixing it with the authentic specimen mentioned below.

As mentioned above and will be described below in detail *o*-tolyl *p*-methylbenzyl ketone was produced by the isomerization of *o*-tolyl *p*-tolyl acetaldehyde and melted at 26°C . when recrystallised from dilute alcohol. (Found: C, 85.8; H, 7.1. $\text{C}_{16}\text{H}_{16}\text{O}$ requires C, 85.7; H, 7.1%). It is slowly oxidised with atmospheric oxygen to *o*- and *p*-toluic acids.

The oxime (0.19 g.) was obtained from the ketone (0.3 g.) by Auers' method, which melted at $96-103^{\circ}\text{C}$. after recrystallisation three times from dilute alcohol. It was subjected to the fractional crystallisation and gave the following fractions:—

Fractions	M.p. ($^{\circ}\text{C}$.)	Yields (in g.)
(1)	109-115	0.06
(2)	77- 84	0.05
(3)	75- 80	0.02

The first fraction (m.p. $109-115^{\circ}\text{C}$.) gave [*p*-tolyl acetyl]-*o*-toluidide by the Beckmann rearrangement indicating the configuration of the oxime as follows:—



[*p*-Tolyl acetyl]-*o*-toluidide was also obtained by the condensation of *p*-tolyl acetic acid and *o*-toluidide in flat needles, m.p. 165°C . (corr.) (Found: N, 5.8. $\text{C}_{10}\text{H}_{17}\text{ON}$ requires N, 5.9%), and the isomeric compound

o-toluyl *p*-methylbenzylamine by the condensation of *o*-toluic acid and *p*-methylbenzylamine in leaflets, m.p. 114°C. (Found: N, 6.1. $C_{16}H_{17}ON$ requires N, 5.9%).

The semicarbazone of *o*-toluyl *p*-methylbenzyl ketone was obtained in the usual way. It crystallised from dilute alcohol in colourless needles, m.p. 172°C. (corr.) (decomp.).

p-Tolyl *o*-methylbenzyl ketone. The ketone (7.5 g.) was obtained by the condensation of *o*-toluyl acetyl chloride (6.5 g.) with toluene (30 c.c.) in the presence of anhydrous aluminium chloride (6 g.) It was recrystallised from dilute alcohol forming colourless scales, 86–87°C. (Found: C, 85.4; H, 7.5. $C_{16}H_{16}O$ requires C, 85.7; H, 7.1%).

o-Tolyl acetyl chloride, obtained from the corresponding acid and thionyl chloride, boiled at 175°C under 28 mm. with slight decomposition. According to P. Hill and W. F. Short⁽⁶⁹⁾ it boils at 106–107°C. under 10 mm. and A. E. Bradfield, B. H. Hedge, B. S. Rao, J. L. Simonsen and A. E. Gillam gave the boiling point 111–112°C. under 16 mm.

The semicarbazone crystallised in bundled needles on the 54th day of standing of the solution of the ketone (0.9 g.), semicarbazide hydrochloride (0.9 g.) and potassium acetate (0.9 g.) in dilute alcohol (10 c.c. of 95% alcohol mixed with 4 c.c. of water). It was recrystallised from dilute alcohol in colourless needles, m.p. 185–186°C. (corr.) (decomp.) (Found: N, 6.3. $C_{16}H_{17}ON$ requires N, 5.9%).

Isomerization of o-tolyl p-tolyl acetaldehyde. The aldehyde (15.0 g.) was passed on the Japanese acid earth (25 g.) heated at 300°C. at a rate of 3.3 g. per hour being accompanied by the slow flow of carbon dioxide. A heavy yellowish oil (a) mixed with drops of water (8.8 g. in total) was collected in the receiver in the course of the passing and during the lapse of 1 hour after the passing of all of the aldehyde into the reaction tube. The tube was then evacuated at 300°C. and 0.9 g. of a yellow oil (b) were obtained. When the temperature was raised to 350°C. under the reduced pressure, 0.1 g. of a reddish viscous oil (c) came out. All (a), (b) and (c) showed no colour reaction characteristic to aldehydes.

The product (a) was freed from the water drops with anhydrous sodium sulphate and distilled, giving a fraction (0.9 g.) which boiled at 100–115°C. obviously consisting of mainly toluene. The residue (7.3 g.) was distilled under the reduced pressure of 4 mm. giving the fractions shown in Table 3.

Table 3.

Fractions	B.p. (°C.)	Yields (g.)	Remarks
(1)	145–165	1.3	Yellow oil with aromatic odour.
(2)	165–172	0.9	„
(3)	172–180	3.6	Yellow viscous oil, odourless.
(4)	Residue	1.5	„

(69) *J. Chem. Soc.*, 1935, 1125.(70) *Ibid.*, 1936, 675.

The fractions (1) and (2) in Table 3 manifested no apparent change when cooled at -15°C . for 21 hours. The fraction (3) was converted to a mush when similarly treated, which melted on touching with the hand. It was recrystallised from dilute alcohol in colourless columns, m.p. 26°C ., and confirmed to be *o*-tolyl *p*-methylbenzyl ketone through the Beckmann rearrangement of its oxime as described above.

The fraction (4) was changed to a mush by standing at the ordinary temperature for several days and a small amount of *p*-tolyl *o*-methylbenzyl ketone, m.p. $86\text{--}89^{\circ}\text{C}$., was obtained from it, which was identified by the mixed melting point with the sample synthesised as stated above.

The ratio of the amount of *o*-tolyl *p*-methylbenzyl ketone to that of *p*-tolyl *o*-methylbenzyl ketone, both produced by the isomerisation of *o*-tolyl *p*-tolyl acetaldehyde, was estimated about 4:1.

p-Chlorobenzoyl methyl acetate. Potassium acetate (200 g.) dissolved in alcohol (300 c.c.) was added to *p*-chlor- ω -bromacetophenone (170 g.) dissolved in hot alcohol (500 c.c.) and the mixture was heated for a while and left to stand. On the next day a large amount of potassium bromide was found thrown down, which was filtered and the filtrate concentrated on the water bath and left to cool down to the ordinary temperature: *p*-Chlorobenzoyl methyl acetate (102 g.) separated forming glittering scales, m.p. $71.5\text{--}72.5^{\circ}\text{C}$., when recrystallised from ligroin (b.p. $80\text{--}120^{\circ}\text{C}$.). (Found: Cl, 16.8. $\text{C}_{10}\text{H}_9\text{O}_3\text{Cl}$ requires Cl, 16.7%).

p-Chlorobenzoyl carbinol. Barium carbonate (50 g.) was added to the boiling water (200 c.c.) followed by *p*-chlorobenzoyl methyl acetate (40 g.) and the mixture was boiled for 1 hour. It was filtered hot and the insoluble matter remaining on the filter paper was extracted with hot water, the extract combined with the filtrate. On cooling the combined liquid, *p*-chlorobenzoyl carbinol (28 g.) separated. It was recrystallised from ligroin in colourless needles, m.p. $123\text{--}126^{\circ}\text{C}$. (uncorr.) (decomp.) (Found: Cl, 20.7. $\text{C}_8\text{H}_7\text{O}_2\text{Cl}$ requires Cl, 20.8%).

o-*p*-Chlorophenyl *o*-*p*-tolyl ethylene glycol. *p*-Chlorobenzoyl carbinol (11 g.) was added little by little in the form of crystalline powder to the Grignard reagent prepared from *p*-iodotoluene (50 g.) and magnesium. A vigorous reaction occurred. The reaction mixture was boiled for 2 hours and left to stand overnight. It was treated with cold dilute acetic acid (12 g. of glacial acetic acid in 200 c.c. of ice water). The upper ethereal solution was washed with dilute caustic soda and then with water and the ether was removed. The residue solidified on cooling. It was subjected to the steam distillation, toluene and other volatile impurities being thereby removed. The required glycol remained in the distilling flask, which on cooling solidified to a yellowish mass. It was recrystallised from ligroin in colourless needles (17 g.), m.p. $132\text{--}133^{\circ}\text{C}$. (uncorr.) (Found: Cl, 13.4. $\text{C}_{15}\text{H}_{15}\text{O}_2\text{Cl}$ requires Cl, 13.5%).

The benzoyl derivative obtained by the usual method crystallised from dilute alcohol in fine needles, m.p. $145\text{--}146^{\circ}\text{C}$. Mol. wt. (Rast), 358.2. $\text{C}_{22}\text{H}_{19}\text{O}_3\text{Cl}$ requires 366.5.

p-Chlorophenyl *p*-tolyl acetaldehyde. A mixture of *o*-*p*-chlorophenyl *o*-*p*-tolyl ethylene glycol (40 g.), crystalline oxalic acid (100 g.) and water (40 c.c.) was heated in an oil bath for 3 hours, the slow flow of carbon dioxide being passed into the mixture meanwhile. The tempera-

ture was maintained at 115°C. while that of the oil bath showed 140°C. After cooling the content of the vessel was extracted with ether, the ethereal solution washed with dilute caustic alkali, saturated solution of sodium chloride and with water, dried over calcium chloride. The residual oil (38 g.) obtained by removal of the ether was distilled under

the reduced pressure of 6 mm. giving the results shown in Table 4.

Table 4.

Fractions	B.p. (°C.)	Yields (g.)
(1)	150-197	2.2
(2)	197-200	20.9
(3)	Residue	11.0

fuchsin-sulphurous-acid solution with blue colour. It is oxidized slowly in the presence of air and light at the ordinary temperature to produce *p*-chlorophenyl acetic acid. The semicarbazone prepared in the usual way dissolved difficultly in dilute alcohol; it was recrystallised from a mixture of toluene and ligroin (1:1) in white powder, m.p. 159-160°C. (uncorr.) (to a yellow melt). (Found: N, 14.1. $C_{16}H_{16}ON_3Cl$ requires N, 13.9%).

p-Chlorophenyl *p*-tolyl acetic acid. The acid (1.3 g.) was obtained from *p*-chlorophenyl *p*-tolyl acetaldehyde (4.0 g.) by the method similar to that employed for the oxidation of *o*-tolyl *p*-tolyl acetaldehyde. It was recrystallised from ligroin in clustered needles in stellar form, m.p. 145.5°C. (uncorr.). (Found: Cl, 13.4; Mol. wt. (by titration with 1/20 N sodium hydroxide), 261.5. $C_{15}H_{13}O_2Cl$ requires Cl, 13.6%; Mol. wt., 260.5).

p-Chlorophenyl *p*-tolyl ketone. (a) *a*-*p*-Chlorophenyl *a*-*p*-tolyl ethylene glycol (0.30 g.) was dissolved in 80% acetic acid (20 c.c.) and chromic oxide (0.32 g. dissolved in a small quantity of water) was added to the solution and the mixture was left to stand overnight. It was heated on the water bath for 20 minutes and cooled. Glittering scales (0.25 g.) crystallised out, of which the amount increased on the addition of water. It was separated by filtration, washed with water and recrystallised from dilute alcohol in colourless scales, m.p. 128-129°C. (uncorr.) (Found: Cl, 15.3. $C_{14}H_{11}OCl$ requires Cl, 15.4%).

(b) *p*-Tolyl acetyl chloride (4.0 g.) was condensed with chlorobenzene in the presence of anhydrous aluminium chloride and the required ketone (0.36 g.) thus obtained was recrystallised from dilute alcohol in faintly reddish scales.

(c) When *p*-chlorophenyl *p*-tolyl acetaldehyde was purified through the addition compound of sodium bisulphite a small amount of a substance very difficult to react with the bisulphite was obtained which was confirmed to be *p*-chlorophenyl *p*-tolyl ketone.

(d) On long standing *p*-chlorophenyl *p*-tolyl acetaldehyde was partly changed to *p*-chlorophenyl *p*-tolyl ketone.

All the four specimens described above showed the same melting point which was not depressed when mixed with one another. W. D.

Cohen⁽⁷¹⁾ obtained the same ketone by the condensation of *p*-chlorobenzoyl chloride and toluene and gave the melting point 118°C. (very probably a typographical error for 128°C.).

p-Tolyl *p*-chlorobenzyl ketone. Phenyl acetic acid (22 g.) was nitrated following the information given by W. Borsche⁽⁷²⁾ resulting in *p*-nitrophenyl acetic acid (15 g.) which on reduction by the method described in "Organic Syntheses"⁽⁷³⁾ gave *p*-aminophenyl acetic acid (10.4 g.). The amino acid was changed to *p*-chlorophenyl acetic acid (4.0 g.) and then to *p*-chlorophenyl acetyl chloride (4.0 g.) which was condensed with toluene (20 c.c.) in the presence of anhydrous aluminium chloride (6 g.). The reaction mixture was treated with ice water and the crystals thereby separating (6.0 g.) were recrystallised from dilute alcohol in colourless glittering plates, m.p. 113.5°C. (uncorr.). (Found: Cl, 14.4. $C_{15}H_{13}OCl$ requires Cl, 14.5%). L. Szëgo and P. Ostinelli⁽⁷⁴⁾ gave the melting point 113°C. Attempts to obtain the ketone from *p*-methyl ω -bromacetophenone and chlorobenzene resulted in no good result.

The semicarbazone prepared in the usual way formed colourless needles m.p. 191–192°C. (uncorr.) (decomp.). (Found: N, 5.5. $C_{15}H_{14}ONCl$ requires N, 5.4%). The oxime was prepared in the usual way. It was recrystallised from dilute alcohol in glittering plates, m.p. 136–137°C (uncorr.). (Found: N, 5.5. $C_{15}H_{14}ONCl$ requires N, 5.4%).

p-Chlorophenyl *p*-methylbenzyl ketone. The raw *p*-tolyl acetyl chloride prepared from *p*-tolyl acetic acid (4 g.) and thionyl chloride (12 g.) was added drop by drop to chlorobenzene (20 c.c.) mixed with anhydrous aluminium chloride (6 g.), the mixture being cooled with ice water meanwhile. After 4 hours' standing, it was treated with ice water, washed with dilute alkali and then with water, dried over calcium chloride and the excess chlorobenzene was removed leaving resinous brown mass (4 g.), which was recrystallised from dilute alcohol in colourless scales (1.2 g.), m.p. 103.5°C. (Found: Cl, 14.6. $C_{15}H_{13}OCl$ requires Cl, 14.5%). L. Szëgo and P. Ostinelli⁽⁷⁵⁾ gave the melting point 123°C.

The semicarbazone crystallised from dilute alcohol in colourless needles, m.p. 151–152°C. (Found: N, 13.9. $C_{16}H_{16}ON_3Cl$ requires N, 13.9%). The oxime crystallised from dilute alcohol in colourless needles, m.p. 106–107°C. (Found: N, 5.7. $C_{15}H_{14}ONCl$ requires N, 5.4%).

Isomerization of p-chlorophenyl p-tolyl acetaldehyde. The aldehyde (18.0 g.) was passed on the Japanese acid earth (25 g.) heated at 300°C at a rate of 4.5 g. per hour, being accompanied by the slow current of carbon dioxide. A yellow oil (a) mixed with a small amount of crystals (1.6 g. in total) was first collected and then a viscous yellow oil (b) (4.5 g.) came out which soon solidified on cooling. By evacuating the reaction tube at the same temperature a blackish oil (c) (4.5 g.) was obtained which likewise solidified at once. The product (b) was separated into two parts by fractional crystallisation from ligroin, i.e., (i) (3.0 g.) less soluble in the solvent and (ii) (1.5 g.) more soluble in it. The product

(71) *Rec. Trav. Chim. Pays-Bas.*, **38** (1919), 117.

(72) *Ber.*, **42** (1909), 3596.

(73) *Coll. Vol. I*, (1932), 44.

(74) *Gazz. chim. ital.*, **60** (1930), 677; *Chem., Abst.*, **25** (1931), 1524.

(75) *Loc. cit.*

(i) was recrystallised once more from ligroin forming colourless scales (2.7 g.) melting at 104–105.5°, from which the following fractions were obtained by fractional crystallisation three times from ligroin:—

Table 5.

Fractions	Yields (g.)	M.p. (°C.)	Thawing point (°C.)	Remarks
(1)	2.31	105.6	103	Colourless scales.
(2)	0.20	104	101	„ „
(3)	0.15	95–98	—	Yellowish scales.
(4)	0.02	170–195	—	Colourless powder.

The fraction (1) in Table 5 may safely be stated to consist of *p*-chlorophenyl *p*-methylbenzyl ketone (ca. 80%) and *p*-tolyl *p*-chlorobenzyl ketone (ca. 20%) by referring it to Fig. 1. (p. 201). The fraction (1) melted at 103.5–104°C. when mixed with the former ketone (m.p. 103.5°C.) and at 108°C. with the latter (m.p. 113.5°C.). The fraction (2) is richer in *p*-chlorophenyl *p*-methylbenzyl ketone than the fraction (1). The fraction (3) is obviously very impure, and the fraction (4) was not further studied of which the melting point was found much higher than those of both the above ketones.

The product (ii) mainly consisted of oily substance mixed with a small quantity of solid matter which was recrystallised several times from dilute alcohol forming colourless glittering scales (0.15 g), m.p. 101°C.; thawing point, ca. 85°C, probably *p*-chlorophenyl *p*-methylbenzyl ketone mixed with a small quantity of impurities.

The product (c) was treated similarly to (b); it was first separated into two parts, i.e., (i) (3.0 g.) less soluble in ligroin, m.p. 100–104°C. and (ii) (1.5 g.) more soluble in it. The part (i) was once more recrystallised from ligroin forming light yellow scales which melted at 106.5–107.5°C. alone, and at 105–106°C. when mixed with pure *p*-chlorophenyl *p*-methylbenzyl ketone (m.p. 103.5°C.), revealing the composition of 59% of this ketone and 41% of *p*-tolyl *p*-chlorobenzyl ketone. It was recrystallised several times from dilute alcohol giving the following fractions:—

Table 6.

Fractions	Yields (g.)	M.p. (°C.)	Thawing point (°C.)	Remarks
(1)	0.02	107.5	106.7	—
(2)	1.34	108.0	107.1	Yellowish scales.
(3)	0.31	107.0	106.0	Colorless scales.
(4)	6.27	104.3	102.0	Yellow scales.
(5)	0.09	95–99.5	—	—

0.4 g. of the fraction (2) in Table 6 gave the oxime (0.3 g.) which was fractionated over ten times affording colourless needles (0.09 g.), m.p. 106–107°C. alone or mixed with *p*-chlorophenyl *p*-methylbenzyl ketoxime, and a small quantity of needles which melted alone at 122–126°C., and at 128–134°C. when mixed with *p*-tolyl *p*-chlorobenzyl ketoxime (m.p. 136–137°C.). By the repeated fractional crystallisation of the semicarbazone obtained from the fraction (2) in Table 6, a small quantity of a fraction was obtained which melted at 187–189°C. alone, and at 188–189°C. when mixed with the semicarbazone of *p*-tolyl *p*-chlorobenzyl ketone (m.p. 191–192°C.).

More soluble part of the product (c), (p. 300) was recrystallised several times from dilute alcohol and gave 0.62 g. of yellowish scales melting at about 96°C. and 0.04 g. of yellowish scales melting at about 95°C. Both may very probably be impure *p*-chlorophenyl *p*-methylbenzyl ketone.

Summary.

(1) All the phenomena hitherto ascribed to the characteristic catalytic action of Japanese acid earth can be explained by taking its strong electron-seeking property into consideration. Thus its ability to promote the hydrolysis of cane sugar or starch and the oxidation of pyrogallol and its property to give various oxidase-like colour reactions are all due to its selective adsorptive power for hydroxyl ion. The facts can similarly be explained that the dehydration or deamination of various organic compounds takes place through its catalytic action followed by the intramolecular rearrangement, as observed in the reaction of producing cyclopentane derivatives from cyclohexanol, cyclohexylamine or their methyl derivatives.

The initial step of the formation of β,β' -dinaphthyl from naphthalene in the presence of the earth is the polarisation of the naphthalene molecule promoted by its electron-seeking property.

(2) Several diarylacetaldehydes have been newly synthesised and found to rearrange themselves to give the corresponding ketones, when heated at 300°C. in the presence of the earth. Thus phenyl *p*-tolyl and *m*-tolyl *p*-tolyl acetaldehydes gave phenyl *p*-methylbenzyl and *m*-tolyl *p*-methylbenzyl ketones respectively, while *o*-tolyl *p*-tolyl and *p*-tolyl *p*-chlorophenyl acetaldehydes gave the respective mixtures of *o*-tolyl *p*-methylbenzyl and *p*-tolyl *o*-methylbenzyl ketones and of *p*-chlorophenyl *p*-methylbenzyl and *p*-tolyl *p*-chlorobenzyl ketones.

(3) By comparing the yields in the isomeric ketones thus produced the order of the facility of separation of the different aryl groups was determined as follows:—

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

The phenyl group may most probably have the greater migratory tendency than the *m*-tolyl.

(4) The mechanism of the conversion of the aldehydes to the ketones has been discussed. It has been postulated that an electromeric displacement of electrons in the carbonyl group $\overset{\curvearrowright}{\text{C}}=\text{O}$ is promoted by the

action of the earth, and one of the aryl groups migrates with its valency electrons from the adjacent α -carbon atom to the depleted carbonyl carbon. A proton is then splitted from the carbonyl carbon and unites with the carbonyl oxygen to give the enolic form of the ketone, isomeric to the aldehyde. The conclusion has been reached that the more electron-attracting of the two aryl groups must be first separated as anion.

(5) It was confirmed that the capacity of the *p*-tolyl group for electron-release is much larger than those of *o*-tolyl, *m*-tolyl, phenyl and *p*-chlorophenyl groups. By these results a new chemical evidence has been given for the tautomeric effect of the methyl group.

(6) Following compounds have been newly synthesised and their constitutions were confirmed:— *a*-phenyl *a*-*p*-tolyl, *a*-*m*-tolyl *a*-*p*-tolyl, *a*-*o*-tolyl *a*-*p*-tolyl and *a*-*p*-chlorophenyl *a*-*p*-tolyl ethylene glycols and their benzoyl derivatives; *p*-tolyl *m*-methylbenzyl, *m*-tolyl *p*-methylbenzyl, *o*-tolyl *p*-methylbenzyl, *p*-tolyl *o*-methylbenzyl, *p*-chlorophenyl *p*-methylbenzyl and *p*-tolyl *p*-chlorobenzyl ketones and their oximes and semicarbazones; *m*-tolyl *p*-tolyl, *o*-tolyl *p*-tolyl and *p*-tolyl *p*-chlorophenyl acetic acids; *p*-methylbenzoyl carbinol, *p*-chlorobenzoyl methyl acetate and *p*-chlorobenzoyl carbinol.

(7) *o*-Tolyl *p*-methylbenzyl and *m*-tolyl *p*-methylbenzyl ketones have been found to be oxidised slowly by the action of atmospheric oxygen on long standing, giving the mixtures of *o*-toluic and *p*-toluic acids and of *m*-toluic and *p*-toluic acids respectively, while the isomeric ketones, *p*-tolyl *o*-methylbenzyl and *p*-tolyl *m*-methylbenzyl ketones remained unchanged.

(8) The stereo-isomers of the oximes of the following ketones were isolated and their configurations were determined by carrying out the Beckmann rearrangement:— *m*-tolyl *p*-tolyl, *m*-tolyl *p*-methylbenzyl and *o*-tolyl *p*-methylbenzyl ketones.

For the identification of the products of the rearrangement the following compounds were newly synthesised:— *p*-toluyl *m*-toluidide, *m*-toluyl *p*-toluidide, [*p*-tolyl acetyl]-*m*-toluidide, *m*-toluyl *p*-methylbenzylamine, [*p*-tolyl acetyl]-*o*-toluidide and *o*-toluyl *p*-methylbenzylamine.

(9) α , β -Dibenzoyl ethane was confirmed to occur in the reaction product when ω -bromacetophenone was condensed with toluene by the Friedel and Crafts' reaction. The anticipated phenyl *p*-methylbenzyl ketone has not been isolated from the reaction product.

(10) It was found that the considerable quantity of *m*-tolyl *p*-tolyl ketone was produced when *m*-tolyl *p*-tolyl acetaldehyde is purified through its bisulphite compound or oxidised with moist silver oxide.

Similar facts have been observed in the cases of *o*-tolyl *p*-tolyl and *p*-chlorophenyl *p*-tolyl ketones. They were produced in the course of the purification of *o*-tolyl *p*-tolyl and *p*-chlorophenyl *p*-tolyl acetaldehydes respectively through the addition compounds of sodium bisulphite and by the autoxidation of the above-mentioned aldehydes on long standing in the presence of light and air.

(11) The semicarbazones of several above-mentioned ketones have been found very difficult to be produced. Thus the semicarbazone of *m*-tolyl *p*-tolyl ketone was formed after 22 days' standing of the dilute alcoholic solution of the ketone mixed with semicarbazide hydrochloride and potassium hydroxide and that of *p*-tolyl *o*-methylbenzyl ketone only

after 54 days. The semicarbazone of *m*-tolyl *p*-methylbenzyl ketone was not confirmed to produce even after 140 days' standing of the reaction mixture.

(12) Equilibrium diagrams of the systems of phenyl *p*-methylbenzyl and *p*-tolyl benzyl ketones and of *p*-chlorophenyl *p*-methylbenzyl and *p*-tolyl *p*-chlorobenzyl ketones have been drawn by applying the modified Rheinboldt's method. It was found that an eutectic point exists in the former system while a solid solution is formed in the latter. (*Concluded*).

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